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THE ALLOTROPY OF CADMIUM.

By Ernst Cohen.

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1. Some time ago Frederick H. Getman published a paper[1] on the allotropy of cadmium in which he describes some experiments bearing upon my investigations on this subject. However, in Getman's assumptions as well as in the conclusions he deduces from his careful experimental work some mistakes have crept in. In the present paper we intend to prove that if these mistakes are removed, Getman's results become identical with those of Cohen and Helderman. As a result Getman's work affords a very welcome control as well as confirmation of the results formerly got by ourselves.

2. Having found in our dilatometric experiments that there exist three (at least) different modifications of cadmium to which the names Cd_α, Cd_β and Cd_γ, respectively, were given, we stated that the transition temperature of the transformation

$$Cd_\alpha \rightleftarrows Cd_\beta$$

is to be found in the vicinity of 60°. We were unable until now to fix this temperature more closely with the dilatometer in consequence of the presence of Cd_γ.

[1] This Journal, 39, 1806 (1917).

3. Getman prepared in the same way as we did a number of Hulett cells, which were constructed according to the scheme

Cd	Solution of $CdSO_4.{}^8/_3H_2O$ $^1/_2$ saturated at 20°	Cd amalgam x% by weight

Whereas x was generally 12.5 in our cells, Getman has chosen $x = 8$. The negative electrode consisted of a platinum spiral covered with an electrolytic deposit of cadmium. If these cells are maintained for some time at 20° they finally give a constant e. m. f. In perfect agreement with our statement Getman found that three different types of cells were formed in this way: 10% of the cells reached the constant value of 50 millivolt at 25° (Cohen and Helderman's γ-cells); 70% of the cells reached the constant value of 48 millivolt at 25° (Cohen and Helderman's β-cells); 20% of the cells reached the constant value of 47 millivolt at 25° (Cohen and Helderman's α-cells).

4. In determining the e. m. f. of these cells between 0° and 40° as a function of temperature, Getman found for the

$$\alpha\text{-cells:}\quad E_\alpha = 0.04742 - 0.000200\ (t - 25). \qquad (1)$$

This is the same equation as has been given by Cohen and Helderman.[1] For the β-cells he found:

$$E_\beta = 0.04862 - 0.000201\ (t - 25). \qquad (2)$$

These cells have not been investigated in this direction by Cohen and Helderman. Finally Getman deduces for the γ-cells:

$$E_\gamma = 0.05047 - 0.0002437\ (t - 25) \qquad (3)$$

which is the same formula as that found by Hulett.

5. Concerning the behavior of the cells above 40° Getman says:

"On raising the temperature of the cells above 40°, the temperature coefficients were found to undergo a reversal of sign. The values of the e. m. f. given by the different cells when maintained for a short time at a temperature above 40° were found to be quite divergent. On prolonged standing at this temperature, however, the divergence in e. m. f. was found to disappear and final equilibrium values agreeing within the limits of experimental error were obtained. It was found that stabilization between 40° and 80° could be brought about more quickly by maintaining the cells at a temperature of 95° for several days. From the data obtained with five cells which had been stabilized in this manner an interpolation formula,[2]

$$E = 0.04280 + 0.000170\ (t - 25), \qquad (4)$$

was derived by the method of least squares. On applying this formula to the data obtained with other cells, satisfactory agreement between the observed and calculated values of e. m. f. was secured."

6. After having rightly pointed out that this discontinuity in the curves mentioned above cannot be ascribed to any abrupt change in the behavior

[1] *Proceedings Koninklijke Akademie van Wetenschappen te Amsterdam*, **17**, 1050 (1915).

[2] THIS JOURNAL, **39**, note on page 1811 (1917).

of the half-saturated solution of cadmium sulfate, Getman continues as follows:[1]

> "That the discontinuity cannot be ascribed to any change in the amalgam has been proved by the investigations of Bijl,[2] in which the e. m. f. of a cell formed by connecting an 8% cadmium amalgam with a standard electrode was found to *decrease regularly* as the temperature was raised from 25° to 75°."

Consequently he ascribes this discontinuity to the transformation of Cd_α into Cd_β in the vicinity of 40°, calculating the transition temperature t by equating the formulas (1) and (4):

$$0.04742 - 0.000200\,(t - 25) = 0.04280 + 0.000170\,(t - 25),$$

from which he finds

$$t = 37.49°,$$

that is to say, whereas Cohen and Helderman found that Cd_α changes into another modification (Cd_β) in the vicinity of 60°, Getman considers 37.49° to be the transition temperature of these modifications.

7. In the first place I should like to call the reader's attention to the mistake in that part of Getman's statement, which is given above (paragraph 6) in italics. The *contrary* has been proved quantitatively by Bijl.[3] This is evident from that part of Bijl's diagram which describes the behavior of the 8% amalgam used by Getman in his cells. This amalgam contains 13.4 atomic per cents. of cadmium and the diagram shows that the amalgam passes in the vicinity of 40° from the *heterogeneous* into the *homogeneous liquid* phase. Consequently, cells with a constant negative electrode which contain below 40° the heterogeneous 8% amalgam will show at this temperature an abrupt change of their temperature coefficient.[4] These facts have been overlooked by Getman; the temperature of 37.49° found by him consequently does not correspond to the transition temperature of Cd_α into Cd_β.

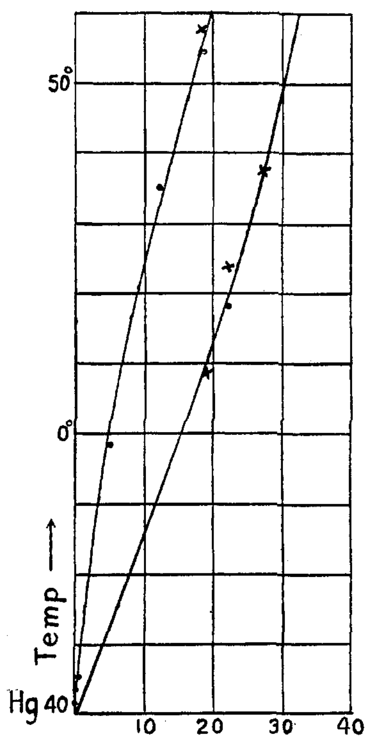

Fig. 1.

8. In order to prove this, it may be

[1] The italics are mine (Cohen).
[2] *Z. phys. Chem.*, **41**, 641 (1902).
[3] *Ibid.*, **41**, 641 (1902).
[4] Ernst Cohen and H. R. Kruyt, *Ibid.*, **72**, 84 (1910).

borne in mind that Getman investigated some β-cells between 0° and 35° in which Cd_β had been generated by maintaining at 20° some cadmium which had been electrolytically deposited on a platinum spiral. According to Getman's measurements for these β-cells our Formula 2 holds good between 0° and 35°. On the other hand, Getman investigated similar cells above 40°, but the Cd_β which they contained had been formed by heating α- (or γ-) cells at a temperature of 95° for several days, the cadmium thus being in contact with a solution of cadmium sulfate. According to Getman's measurements above 40° our Formula 4 holds good for these cells. Whereas the elements contained the *heterogeneous* amalgam as long as they were at temperatures below 40°, they contained the *homogeneous liquid* phase above this temperature.

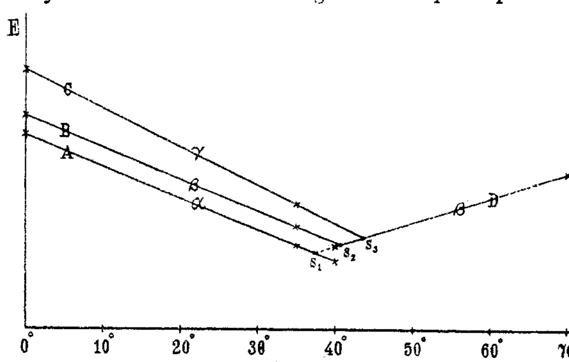

Fig. 2.

The temperature at which the e. m. fs. of these two types of cells become identical corresponds to the temperature at which the heterogeneous phase of the 8% amalgam changes into the *homogeneous liquid* state. If the electrical measurements of Getman are accurate, the point of intersection S_2 of the curves B and D should be found at the temperature indicated by Bijl's diagram, *viz.*, 40°.

From Getman's equations,

$$0.04862 - 0.000200\ (t - 25) = 0.004280 + 0.000170\ (t - 25),$$

we find in perfect agreement with Bijl's results

$$t = 40.7°.$$

9. We have now to look at the meaning of the temperature of 37.49° found by Getman, which he considers to be the transition temperature of the transformation of Cd_α into Cd_β.

At 37.49° the curves A and D intersect, *viz.*, this is the temperature at which the cells

Cd_α	Solution of $CdSO_4.{}^8/_3H_2O$ $^1/_2$ sat. at 20°	Cd amalgam 8% by weight (*heterogeneous*)

and

Cd_β	Solution of $CdSO_4.{}^8/_3H_2O$ $^1/_2$ sat. at 20°	Cd amalgam 8% by weight (*homogeneous liquid*)

have the same e. m. f. From Fig. 2 we see that this temperature must be lower than that (40.7°) at which the *heterogeneous* amalgam changes into the *homogeneous liquid* state. As a matter of fact it was found by Getman 3° lower. Evidently it does not correspond to the transition temperature of the transformation of Cd_α into Cd_β.

The same may be said with regard to the point of intersection S_3 of the curves C and D. According to Fig. 2 this point is to be found at a temperature above 40.7°. From Getman's measurement we find 43.5°.

10. Getman considering 37.49° as the transition temperature of Cd_α into Cd_β next points out that our dilatometric measurements are open to objection. He says:

"It must be borne in mind, however, that in each of the dilatometric measurements never less than 300 g. of cadmium were used *and it is a well-established fact that when so large a mass of a metal undergoes molecular transformation the true transition temperature may be far removed from that at which the transformation actually takes place.*"

Here again a mistake has crept in. *Ceteris paribus* the accuracy of dilatometric measurements as carried out by ourselves increases with the quantity of material used, as the change of the level in the capillary tube at constant temperature increases with this quantity. Moreover, the fact that the direction in which the oil moves shows a reversal of sign[1] if the temperature increases only 0.5°, proves that any retardation of the transformation has not taken place. It must be borne in mind that our metal had always been treated with the solution of an electrolyte in order to exclude retardation. Neither my own experience in this field of research nor that of others mentioned in the literature agrees with Getman's statement which has been given above in italics.

11. We shall consider now another part of Getman's paper. He also repeated the experiments carried out by Cohen and Helderman in order to prove in another way the reality of existence of Cd_β. About this part of our investigations we have written:[2] In order to ascertain if the e. m. f. of the β-cells has a real significance, experiments may be carried out on the following lines: At temperatures above the transition point of the transformation $Cd_\alpha \rightleftarrows Cd_\beta$ (which we found to lie in the vicinity of 60° by dilatometric measurements) the e. m. f. of α-cells must be higher than that of β-cells. After cooling the cells below the transition point mentioned, the contrary will be the case. Our experiments 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°, attained constant e. m. f. of 0.047 volt (at 25.0°) after 4 weeks at 47.5°. We combined this cell (No. 7) with another (No. 22), the e. m. f. of which was 0.048 volt at 25.0°. The 2 cells AB (No. 7) and CD (No. 22) were connected by a siphon, H, which contained the *same* solution of cadmium sulfate as

[1] *Proceedings Koninklijke Akademie v. Wetenschappen te Amsterdam*, **16**, 485 (1913).

[2] *Ibid.*, **17**, 638 (1914); *Z. phys. Chem.*, **89**, 493 (1915); *Trans. Faraday Soc.*, **10**, 216 (1915).

was present in the cells (Fig. 3). The lateral tube E of the siphon was closed by a rubber tube, F, in which was put a glass rod, G. The entire apparatus was brought into a thermostat which could be kept at will at 25.0° or 64.5°. We measured the e. m. f. between the cadmium which had been electrolytically desposited on the platinum spirals A and C 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% by weight does not form a heterogeneous system at 64.5°, its e. m. f. is thus a function of its composition. The use of *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. In this way we found:

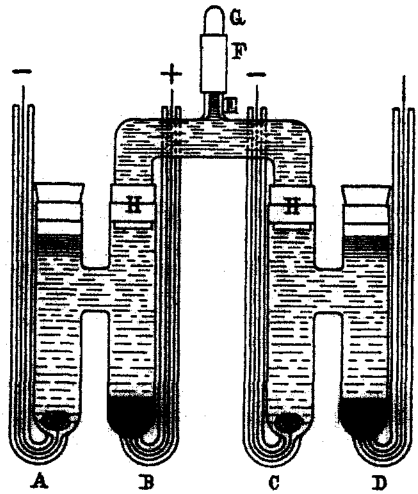

Fig. 3.

	E. m. f. at 25.0°.	E. m. f. at 64.5°.	E. m. f. at 25.0°.
Cell 7	0.04741	0.04029	0.04741
Cell 22	0.04815	0.03979	0.04806

A second experiment with two cells (Nos. 4 and 8), newly constructed, gave the following results:

	E. m. f. at 25.0°.	E. m. f. at 64.5°.	E. m. f. at 25.0°.
Cell 8	0.04757	0.04737	0.04776
Cell 4	0.04839	0.04633	0.04789

Getman, on repeating these experiments,[1] got the same results, *viz.*, there takes place an inversion of poles, if the cells are measured at the temperatures indicated above. This is shown by the following measurements of Getman:

	E. m. f. at 25.0°.	E. m. f. at 64.5°.	E. m. f. at 25.0°.
Cell B-1	0.04729	0.04734	0.04772
Cell A-1	0.04823	0.04652	0.04822

With reference to these results Getman says:

"It will be observed that at 64.5°, the e. m. f. of cells 7, 8 and B-1 was greater than that of cells 22, 4 and A-1, whereas at 25° the e. m. f. of the latter group of cells was greater than that of the former. From this inversion of poles Cohen concluded that an actual transformation of Cdα into Cdβ occurs in the neighborhood of 60°."

[1] The fact that Getman used cells which contained an 8% amalgam, whereas the amalgam of our cells contained 12.5% of cadmium, does not matter *here*, as both these amalgams are *heterogeneous* at 25.0° and *homogeneous liquid* at 64.5°.

Again a mistake has crept in into Getman's statement. Evidently we are not allowed to conclude from this inversion of poles that a transition point exists in the vicinity of 60°; the e. m. f. of the cells has not been measured at a sufficient number of different temperatures between 25° and 64.5°. We only concluded from our experiments that the value of the e. m. f. of our β-cells (48 millivolt at 25°) has a real significance and has to be ascribed to the existence of Cd_β in connection with our pycnometric and dilatometric measurements.

12. With regard to the sentence "from this inversion of poles Cohen concluded than an actual transformation of Cd_α into Cd_β occurs in the neighborhood of 60°," mentioned above, Getman writes:

> "The author's data for cells A-1 and B-1 appear to confirm this conclusion, but when the e. m. f. of these cells was determined at close intervals of temperatures from 0 to 70° no evidence of a transition temperature in the vicinity of 60° was obtained. On the other hand, distinct discontinuities in the e. m. f.-temperature curves were obtained at 39° with A-1 and at 36.8° with B-1. Since the agreement between Cohen's cells and the author's at 25° and 64.5° is satisfactory, it is highly probable that equally close agreement would have been obtained at other temperatures and that had Cohen measured his cells over a wider range of temperatures and plotted the values of e. m. f. against the temperatures he would have obtained no evidence of a transition point at 60°."

There is a mistake in this conclusion, as we shall now demonstrate. Cohen and Helderman's experiments as well as those of Getman which have been described in Paragraph 11 have been carried out on the assumption (the correctness of which has been proved by the measurements) that Cd_α may be heated above its transition temperature without transformation into Cd_β, nay, what is more, it would have been impossible to carry out the measurements if there had not taken place a strongly marked retardation. Consequently it is obvious that Getman could not find a transition point using his B-1 cell (which contained Cd_α) in the manner he described.

On the other hand, also his A-1 cell, which contained Cd_β at all temperatures between 0° and 70°, could not show a discontinuity at 60°.

Moreover, we see from Fig. 2 that the discontinuity of the e. m. f. of cell B-1 which contained Cd_α must occur at a lower temperature than that of cell A-1 where Cd_β is present. As a matter of fact Getman got this result. With the B-1 cell this temperature is 36.8°, with the A-1 cell it was found to be 39°.[1] The discontinuity itself has nothing to do with the transformation of Cd_α into Cd_β but again is to be ascribed to the change of the *heterogeneous* phase of the amalgam into the *homogeneous liquid* one.

13. Finally I want to point out a mistake which has been made where Getman proposes the question whether there exist more than two modi-

[1] That these temperatures have not been found to be 37.49° and 40.7°, respectively, may probably be ascribed to the fact that only one single cell has been used in this case. On the other hand, a small difference in the composition of the positive poles of the cells may have been the cause of this deviation.

fications of cadmium between 0° and 100°. Cohen and Helderman deduced from Equations 1 and 3 found by them (as well as by Getman) for their α- and γ-cells, respectively, that the *metastable* transition point $Cd_\gamma \longrightarrow Cd_\alpha$ lies at 94.8°.

Although we know that the transition temperature of $Cd_\alpha \rightleftarrows Cd_\beta$ lies between 0° and 100°, we are not allowed to conclude that there exist more than 2 *stable* modifications within this range of temperatures. We found that the γ modification is always *metastable* within this range and Getman who used this modification in his γ-cells evidently agrees with this opinion. Consequently his words: "the results of the present investigation, however, seem to render the existence of more than two allotropic modifications of cadmium between 0° and 100° extremely doubtful," lose their significance. Three different forms of cadmium may exist between 0° and 100° but one of these (Cd_γ) is always *metastable* within this range of temperatures.

Summary.

1. It has been demonstrated that in the assumptions made by Getman in his paper on the allotropy of cadmium some mistakes have crept in. Consequently the conclusions which he has drawn from his careful experimental work ought to be revised.

2. If these mistakes are removed Getman's results become identical with those obtained by Cohen and Helderman. In this way Getman's work has been a very welcome control as well as a confirmation of the results formerly got by ourselves.

UTRECHT, HOLLAND.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

A STUDY OF THE ELECTRICAL CONDUCTANCE OF AQUEOUS PHTHALATE SOLUTIONS.

BY HARRISON E. PATTEN, ALFRED J. JOHNSON AND GERALD H. MAINS.

Received March 5, 1918.

Introduction.

Acid potassium phthalate is an excellent standard in the preparation of solutions with definite hydrogen-ion concentration. The titration curve of phthalic acid shows but a very slight irregularity at the point of neutralization of the first hydrogen ion, so that the hydrogen-ion concentration of a solution decreases regularly with the addition of an alkali, almost until the normal salt is formed. Clark and Lubs[1] have made a study of the hydrogen electrode potentials in 0.1 M solution of acid potassium phthalate with varying amounts of sodium hydroxide and hydrochloric acid, and gives the composition of mixtures differing by intervals of 0.2 P_H for use as standard comparison solutions in the colorimetric

[1] *J. Biol. Chem.*, 25, 479 (1916).