Citation:

E. Cohen & W.D. Helderman, The allotropy of Cadmium. V, in:
KNAW, Proceedings, 17 III, 1914-1915, Amsterdam, 1915, pp. 1050-1054

the higher latitudes. A difference of $0^m.4$ in T corresponds to a difference of 0.00006 in $\frac{1}{2}\rho$. Therefore, if we had used for each latitude its own value of ω or ρ, only the last decimal of r/b would have been affected. In that case, however, we must also dismiss the assumption $B_3 = 0$. Of the true value of B_3 we know nothing, but we can assert with considerable certainty that it will be of the same order of magnitude as the difference between the northern and southern rotations, i. e. that it will, like the other causes of uncertainty discussed above, not exceed the fifth decimal place.

The deviations from the ellipsoid are, of course, far beyond the reach of direct micrometrical measures. In fact they are always below 0".01. The effect on the times of the phenomena of the satellites is, at latitude 60°, $0^s.034$ for satellite I and $0^s.070$ for satellite IV, which also is beyond the accuracy of the observations. Thus for all practical purposes we can treat the surface of Jupiter as a true ellipsoid.

Chemistry. — *"The Allotropy of Cadmium V".* By Prof. ERNST COHEN and W. D. HELDERMAN.

The heat of Transformation in the reaction $Cd(\alpha) \rightleftarrows Cd(\gamma)$.

1. As we pointed out some time ago in our sixth communication on the thermodynamics of standard cells,[1]) in calculating the chemical energy of the WESTON cell we have to take into account that cadmium is able to exist in different allotropic modifications. While this problem will be treated later in full, it may be pointed out here that it is very important to know the quantity of heat which is involved in the reaction

$$Cd(\alpha) \rightleftarrows Cd(\gamma).$$

The investigations to be described here have reference to this problem.

2. Up to the present such a heat of transformation of a metal has only been determined in one single case. Some months ago BRÖNSTED [2]) carried out some measurements on the heat of the transformation

$$\text{grey tin} \rightarrow \text{white tin}.$$

1) Chem. Weekblad **11**, 740 (1914).
2) Zeitschr. f. physik. Chemie **88**, 479 (1914),

He found it to be 532 gram calories per gram atom of tin at 0° C.

3. For several reasons the calorimetric method used by BRÖNSTED cannot be applied to our case. We therefore carried out our experiments with a *Transition Cell* of the sixth kind, which has been described by ERNST COHEN. [1])

This cell is constructed according to the scheme:

Electrode of a metal M in its *stable* modification.	Solution of a salt of M of an arbitrary concentration.	Electrode of the metal M in its *metastable* modification.

4. Hitherto it was impossible to make a quantitative application of this cell, as no metal, having a transition point, was known which exists in an electrically sharply defined condition.

Our measurements will prove that the transformation α-cadmium $\rightleftarrows$ γ-cadmium is especially suitable for such an investigation.

As we have in view the carrying out of some other measurements with our α- and γ-cadmium, we have not brought them together in one single transition cell, but used them as the negative electrodes in cells which were constructed according to the scheme given by HULETT. These cells were studied separately. Consequently our cells were made up as follows:

Cd-α	Unsaturated solution of $CdSO_4$ of an arbitrary concentration	Cadmium amalgam. 8 percent by weight	... (α-cell).

and

Cd-γ	Unsaturated solution of $CdSO_4$ of an arbitrary concentration	Cadmium amalgam. 8 percent by weight.	... (γ-cell).

5. On applying the equation of GIBBS—VON HELMHOLTZ:

$$E_e = \frac{E_c}{n\varepsilon} + T\frac{dE_e}{dT}$$

to the α- and γ-cell separately, we find:

$$(E_e)_\alpha = \frac{(E_c)_\alpha}{n\varepsilon} + T\left(\frac{dE_e}{dT}\right)_\alpha \quad \ldots\ldots (\alpha\text{-cell})$$

and:

$$(E_e)_\gamma = \frac{(E_c)_\gamma}{n\varepsilon} + T\left(\frac{dE_e}{dT}\right)_\gamma \quad \ldots\ldots (\gamma\text{-cell})$$

[1]) Zeitschr. f. physik. Chemie **30**, 623 (1899)

$(E_e)_\alpha$ represents the electric energy of the α-cell at T°; $(E_c)_\alpha$ the quantity of heat which is generated if at T° one gram atom of α-Cadmium is dissolved in an unlimited quantity of cadmium amalgam (8 percent by weight).

The signification of $(E_e)_\gamma$ and $(E_c)_\gamma$ is quite analogous.

6. From our equations we get:

$$(E_c)_\gamma - (E_c)_\alpha = n\varepsilon \left[(E_e)_\gamma - (E_e)_\alpha - T \left\{ \left(\frac{dE_e}{dT}\right)_\gamma - \left(\frac{dE_e}{dT}\right)_\alpha \right\} \right] \quad . \quad (1)$$

The expression on the left represents the heat of transformation which accompanies the change of 1 gram atom γ-cadmium into α-cadmium, i. e. the value to be determined.

Therefore we have only to measure the E.M.F. as well as the temperature coefficients of the α- and γ-cell at T°.

7. As we pointed out some time ago the cells which have been studied by HULETT [1]) are our γ-cells. From his determinations between 0° and 40° C. it follows that

$$(E_e)^{t^0}_\gamma = 0.05047 - 0.0002437\,(t-25)\ Volt \quad . \quad . \quad . \quad . \quad (2)$$

8. We constructed our α-cells starting from γ-cells, in which the γ-cadmium was transformed into α-cadmium.

The way in which these γ-cells were prepared and in which their E. M. F. was determined has been described in full in our third paper on the allotropy of cadmium. [2]) As standard cells we used two WESTON-cells and two CLARK-cells which were standing in a thermostat at 25.°0. The E. M. F. of the WESTON-cell was assumed to be 1.0181 Volt at 25°.0.

The ratio $\left(\frac{\text{E. M. F. CLARK}}{\text{E. M. F. WESTON}}\right)_{25^\circ 0}$ was found to be:

Oct. 31. 1914	1.3948
Dec. 17. 1914	1.3947
Jan. 19. 1915	1.3947

We prepared 11 γ-cells. At 25°.0 their E. M. F. was 0.0504 Volt. After standing for a fortnight at 25°.0 the γ-cadmium was transformed into the β-modification as was shown by the fact that the E. M. F. had decreased to 0.048 Volt at 25°.0. In order to transform the β-modification into α-cadmium we put the cells for a fortnight into a thermostat which was kept at 47°.5 C. We now

1) Trans. Americ. electrochem. Soc. **15**, 435 (1909). HULETT used a 10 percent amalgam (by weight). This is a two-phase system between 0° and 40°.

2) These Proc Vol. XVII p. 122.

put a fresh amalgam into the cells, while a fresh solution of cadmium sulphate was also introduced We found that in 4 cells (out of eleven) the β-cadmium had been transfoımed into the α-modification. The E. M. F. of these cells was 0.0474 Volt at 25°.0. (See our third paper on the allotropy of cadmium).

9. These α-cells were systematically investigated at 25°.0, 20°.0 and 15°.0 respectively, in order to determine their temperature coefficients. Table I contains the results.

The measurements may be represented by the equation

$$(E_e)_{\alpha}^{t^o} = 0{,}04742 - 0{,}000200\,(t-25)\ \text{Volt.} \quad . \quad . \quad . \quad (3)$$

TABLE I.

E. M. F. of α-Cells (Volt).

Date	Temperature	Cell H_2	Cell H_4	Cell H_5	Cell H_6	Mean
Jan. 14	25°.0	0.04751	0.04740	0.04763	0 04758	
15 a.m.	25.0	0.04725	0 04797	0.04710	0.04714	0 04742
15 p.m.	25.0	0.04721	0.04790	0.04710	0.04710	
16	25.0	0.04728	0.04794	0.04731	0.04731	
Jan 18	20°.0	0.04848	0.04837	—	—	
19 a.m.	20.0	0.04843	0.04833	—	—	
19 p.m.	20.0	0.04849	0.04841	—	—	
19 night	20.0	0.04832	0.04836	—	—	0.04841
20	20.0	0.04840	—	—	—	
21	20.0	0.04843	—	0.04850	0.04860	
22	20.0	0.04833	—	0.04833	0.04843	
Jan. 23 am.	15°.0	0.04908	—	0.04944	0.04947	
23 pm.	15.0	0.04925	—	0.04966	0.04968	0.04943
24	15.0	0.04959	—	0.04948	0.04956	
25	15.0	0.04924	—	0.04928	0.04937	
Jan. 25	25°.0	0.04752	—	0.04759	0.04761	

10. The reproducibility of these cells is not less good than that of the γ-cells. Calculating from (3) the E. M. F. of an α-cell at 0° C. the value $(E_e)_\alpha^{0°} = 0.05245$ Volt is found, while a cell which had formerly been measured at 0° C. (see our third paper on the allotropy of cadmium) gave the value 0,05225 Volt. This cell had been prepared at a different time using different materials.

11. In order to calculate the heat of transformation of α-cadmium into γ-cadmium at 18°.0 C. we have to introduce the numerical values into our equation (1).

From (2) we find:

$(E_e)_\gamma^{18°} = 0{,}05217$ Volt.

$$\left(\frac{dE_e}{dT}\right)_\gamma^{18°} = -\,0{,}0002437\,\frac{\text{Volt}}{\text{degree}}.$$

From (3) we get:

$(E)_\alpha^{18°} = 0{,}04885$ Volt.

$$\left(\frac{dE_e}{dT}\right)_\alpha^{18°} = -\,0{,}000200\,\frac{\text{Volt}}{\text{degree}}$$

$$(E_c)_\gamma^{18°} - (E_c)_\alpha^{18°} = [0{,}05217 - 0{,}04885 - 291\,(-0{,}0002437 + $$
$$+\,0{,}000200)]\;46105 = \mathbf{739}\text{ gram calories.}$$

If one gram atom of α-cadmium is transformed into γ-cadmium, the change is accompanied at 18°.0 C. by an absorption of 739 gram calories.

12. It may be pointed out that the temperature at which $(E_e)_\alpha = (E_e)_\gamma$ represents the *metastable* transition point of the reaction α-cadmium $\rightleftarrows$ γ-cadmium.

If we put (2) = (3), we find:

$$0.00305 = 0.0000437\;(t - 25)$$
$$t = 94°{,}8$$

Utrecht, January 1915. VAN 'T HOFF-*Laboratory*.