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derived for an ideal gas, *e. g.* from BOLTZMANN's entropy principle, cf. Suppl. N°. 24*a* § 4, or from the virial theorem. Conversely it necessarily follows from this, that in Fig. 2 the θ_0, ϱ-curve at the small densities must change its direction to one parallel to the ϱ-axis, as is clearly indicated by the point $\varrho = 0.08$.

In conclusion we will return for a moment to the assumption rigidly adhered to in this paper, *viz.* that the presence of the nitrogen molecules does not exert any influence on the distribution of the rotatory energy of the oxygen molecules. The following mechanism would be in accordance with this supposition: the oxygen molecules behave at a collision (at least with the nitrogen molecules) as rigid smooth spheres, they carry a (magnetic) doublet (or have according to Suppl. N°. 32*b* § 7 a magnetic moment in consequence of a rotation about an axis of small moment of inertia with zero-point energy in the temperature region considered); the nitrogen molecules have a structure such that they do not exert a directive force on the oxygen molecules. The object of this suggestion is, however, no other than to show that the assumption mentioned above is not an impossible one.

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

The electromotive behaviour of Cadmium.

1. The dilatometric measurements made with cadmium which had been deposited electrolytically, had shown [1]) that this material is a modification which is not stable at room temperature. This corresponds with the result found by ERNST COHEN and E. GOLDSCHMIDT [2]) in their investigations on the electrolysis of solutions of tin salts. When such a solution is electrolysed below 18° C. there is not formed *grey* tin as might be expected, but the modification which is metastable at this temperature is deposited.

In the following pages we give an abbreviated account on the investigations we have carried out in order to identify the product which is formed during the electrolysis of solutions of cadmium salts.

2. Some years ago HULETT [3]) described "a low voltage standard cell", represented by the following scheme:

[1]) These Proc. p. 54.

[2]) Zeitschr. f. physik. Chemie **50**, 225 (1905).

[3]) Trans. Americ. Electrochem. Society **7**, 353 (1905).

Cd	Solution of cadmium sulphate of arbitrary concentration	Cd-amalgam 12.5% of Cd by weight

The electromotive force of this combination is 0.0505 Volt at 25°.0. The reproducibility is about 0.5 millivolt. The cadmium electrode of this cell has to be electrolytically deposited, as Th. W. RICHARDS and LEWIS [1]) have proved, that only this kind of electrodes give a definite potential. ERNST COHEN and SINNIGE [2]), who used these cells in their piezochemical investigations also found that they are reproduceable.

3. Some points in the construction of such cells which play an important rôle in the experiments, to be described below, may be given here. (Fig. 1 A).

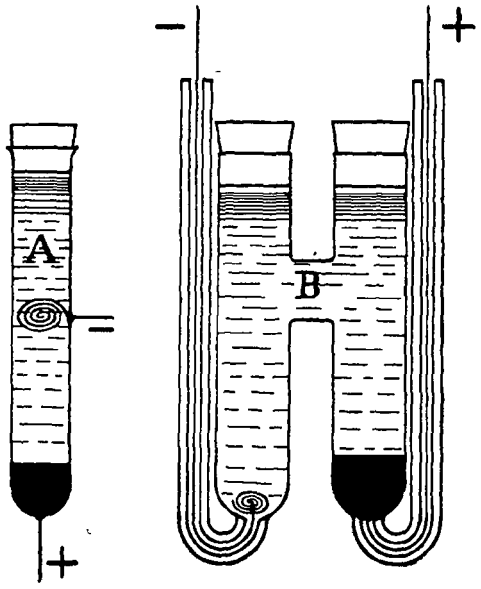

Fig. 1.

The glass part is a thin walled tube about 8—10 mm. in diameter, closed at one end and provided with a platinum wire; two or three centimeters above the closed end is a platinum spiral, with its end fused through the side of the tube (the wires are thoroughly cleaned with aqua regia before filling the cell).

In filling, the spiral is pressed to one side and some 0.5 cc. of 12.5 percent cadmium amalgam is brought into the lower part and melted (carefully avoid bringing the amalgam in contact with the

[1]) Zeitschr. f. physik. Chemie **28**, 1 (1899).
[2]) Zeitschr. f. physik. Chemie **67**, 1 (1909).

platinum spiral). The spiral is then pressed down into a horizontal position. The tube is now filled up with a solution of cadmium sulphate of arbitrary concentration (the E. M. F. of the cell is independent of the strength of the solution).

In order to produce the cadmium electrode a current of 1 or 2 milliamp. (1 or 2 milligrams Cd per hour) is passed from the amalgam to the platinum spiral. At least 18 milligrams must be deposited. The cell may then be sealed off.

4. We specially call attention to the following passage in HULETT's paper: "The electromotive force of these cells is high when the cadmium is freshly deposited, and the length of time required to reach the normal value seems to depend on the thickness of the deposit. Air free cells and those saturated with $Cd(OH)_2$ behave like the others and I have as yet no explanation of the high E. M. F. of newly constructed cells." Our table I shows this decrease of potential of newly constructed cells. It amounts to about 1 millivolt.

TABLE I.

Temperature 25°.0.

E. M. F. in Volts.

Number of cell.	Immediately after formation	After 1 day	After 2 days	After 3 days	After 4 days	After 5 days	After 7 days	After 8 days
a.	0.05156	0.05105	0.05084	0.05078	0.05070	0.05065	0.05052	0.05052
b.	0.05143	0.05099	0.05082	0.05076	0.05068	0.05067	0.05054	0.05056
c.	0.05154	0.05103	0.05084	0.05076	0.05070	0.05067	0.05056	0.05058
d.	0.05151	0.05099	0.05082	0.05076	0.05070	0.05067	0.05056	0.05056
e.	0.05162	0.05113	0.05090	0.05084	0.05074	0.05070	0.05058	0.05058

5. These determinations and those to be described below 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 standardelements (WESTON) were put into a thermostat which was kept at 25°.0. We used as a zero instrument a DESPREZ-D'ARSONVAL galvanometer. It was mounted on a vibration free sus-

pension (JULIUS). The readings were made by means of a telescope and scale; 0.02 millivolt could easily be measured.

6. As it was very important for us to get rid of this variation of E. M. F. we tried to find its cause. We thought it might be found in the electromotive behaviour of the cadmium amalgams, which has been studied particularly by H. C. BIJL [1]).

Fig. 2 contains his results as far as they play a rôle in our investigations. The curves represent the E. M. F. (ordinates) of cells which are constructed according to the following scheme:

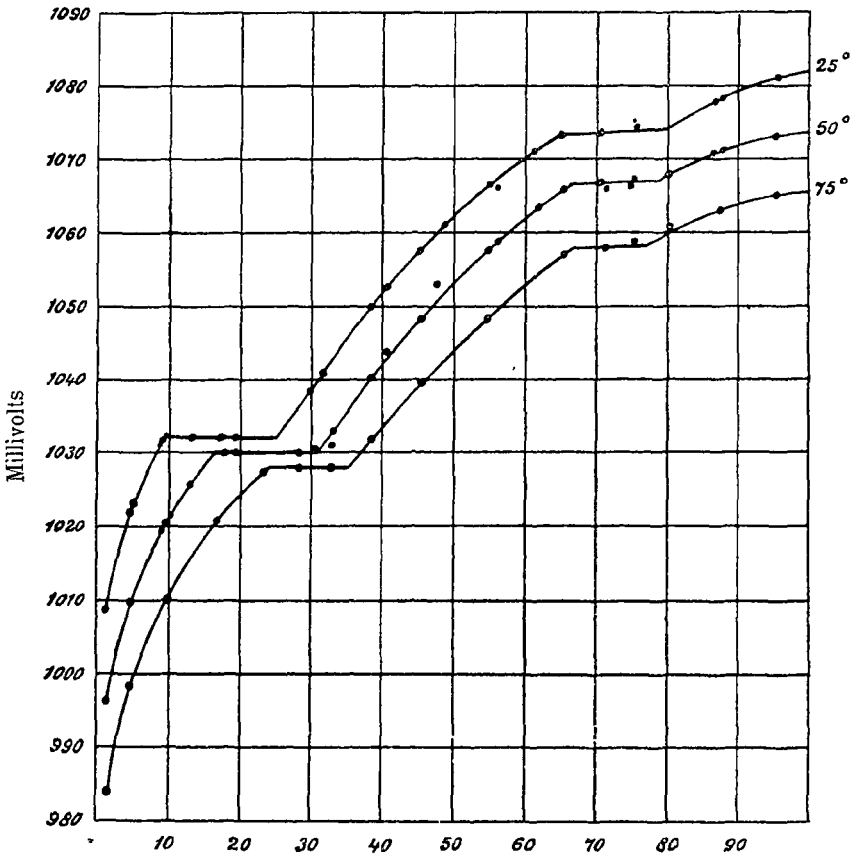

Fig. 2.

Cd-amalgam x-at. Proc.	Solution of cadmium sulphate (765.4 gr. $CdSO_4$ $^8/_3$ H_2O per Litre)	Hg_2SO_4 — Hg

The abscissae represent atom per cents of cadmium.

[1]) Zeitschr. f. physik. Chemie **41**, 641 (1902).

From the drawing it can be seen that the E.M.F. of these cells at 25°.0 is independent of the concentration of the amalgam when its concentration lies between 9.0 and 24.4 at.percents (i. e. 5.9 and 15.4 percent by weight). As soon as the concentration decreases below 5.9% by weight (when we pass from the heterogeneous amalgams to the homogeneous, (c.f. BIJL's paper Fig. 3) the E.M.F. varies with the amount of cadmium present in the amalgam, the potential against pure cadmium *increasing* with *decrease* in the percentage of cadmium.

7. In the light of these facts the high E.M.F. of freshly constructed cells becomes intelligible.

During electrolysis the cadmium which is deposited on the spiral is withdrawn from the upper layer of the 12.5% (or stronger) amalgam, which was originally a two phase system. It is thus possible for this layer to become a monophase system and if this is the case the E.M.F. will *increase* when electrolysis is continued. After the formation of the cell its E.M.F. will then be too high. In the long run cadmium will diffuse to the upper layer: this becomes again a twophase system and the E.M.F. will decrease and finally becomes constant.

8. In order to check this supposition we carried out the following experiment: We put two platinum spirals into the *H*-shaped tube *B* (Fig. 1). Into the right-side tube we put some 1% (by weight) cadmium amalgam (99 parts by weight of mercury, 1 part of cadmium). This amalgam is a fluid monophase system at ordinary temperature. We filled the tubes with a dilute solution of cadmium sulphate (half saturated at 15° C.). After this the cell was formed in the way described above. (1 milliampère).

After having deposited 20 or 25 milligrams of cadmium on the left-hand spiral, the capillary tube on the right was brought into connection with a waterpump in order to remove the amalgam. A number of small pieces of the 12.5% amalgam were then substituted for this.

These cells give at once an E.M.F. of 0.0503 Volt when they are put into a thermostat at 25°·0 C. It is evident that our assumption made above (§ 7) is correct.

9. All the cells we investigated have been produced in the way described; it is now possible to measure their E.M.F. at once without waiting for 8 to 14 days before their becoming constant.

10. Our dilatometric measurements with cadmium which had been

electrolytically deposited gave the result that this material only undergoes transformation at temperatures below 100°, if it has been in contact at 50° (100°) with a solution of cadmium sulphate.

The probable and obvious conclusion is that by electrolysis we get exclusively γ-cadmium, the modification which is stable at high temperatures. If this were the case, the γ-cadmium would be transformed into β-cadmium at 100°, into α-cadmium at 50° in contact with the solution of the sulphate.

If now the γ-modification is really generated by electrolysis, (analogous to what happens with solutions of tin salts) the HULETT cells which have been measured until now would contain this material as the negative electrode.

If this modification happened to be transformed into the modification which is stable at ordinary temperatures and pressures (1 atm.), this would manifest itself by a *decrease* in the E.M.F.

On the one hand we are working in this case under extraordinarily favourable circumstances for stabilisation (change into the α-modification) as the material formed electrolytically is in a very fine state of division and surrounded by an electrolyte, while the quantity which has to undergo transformation is so very small (20 or 30 milligrams), that the transformation, if it occurs, will be finished in a short space of time.

On the other hand, and this is to be borne in mind in researches of this kind, the possibility exists that the transformation which has to take place *spontaneously*, may be suspended, if the metal deposited by electrolysis forms only one single modification, as the germs needed for transformation are then absent.

11. That the stabilisation generally does not occur is shown by our dilatometric observations as well as by many other facts i. e. by the experiments of W. JAEGER,[1]) ERNST COHEN,[2]) BIJL[3]) and HULETT,[4]) who all found the same E.M.F. (50 millivolt at 25° C.) for cells which were constructed according to the scheme:

Cd electrolytically deposited	Solution of cadmium sulphate	Cd-amalgam 12,5 per cent by weight.

How obstinately the transformation may be delayed might also

[1]) Wied. Ann. **65**, 106 (1898).
[2]) Zeitschr. f. physik. Chemie **34**, 612 (1900).
[3]) Zeitschr. f. physik. Chemie **41**, 641 (1902).
[4]) Trans. Amer. Electrochem. Soc. **7**, 333 (1905).

be inferred from HULETT's[1]) words: "many of these cells are still in good order after five years."

This would be in perfect accordance with our own experiences: CLARK-cells which contain $ZnSO_4 . 6 H_2O$ as solid depolariser preserved their E.M.F. for five years notwithstanding their having been standing at room temperature, i. e. 25 degrees below the transition point of $ZnSO_4 . 6 H_2O$. As in the case of HULLET's cells they had been sealed up after formation.

12. On account of these observations it might be expected that even under circumstances favourable to a transformation (stabilisation) of the negative electrode only a certain number of HULETT cells would show the transformation.

On December 11th 1913 we prepared three H.C. (N°. 1, 2 and 5) in the way described above (§ 3) at room temperature (30 mgr. Cd on the spirals). We then substituted a 12 5 percent cadmiumamalgam for the 1 percent. The E M.F was now 0.0503 Volt. After standing for two months at room temperature the cells were measured again on February 26th 1914. The E M.F. of 1, 2 and 5 had *decreased* to 0 0475 Volt at 25°.0 C. and this value remained unchanged. As might have been expected the E.M.F. had *decreased* by stabilisation of the cadmium.

13. We prepared two new cells (nos. 6 and 7) in the same way as 1, 2, and 5. Immediately after the preparation their E.M F. were 0.04847 and 0 04795 Volt respectively Some days later these values became constant: 0.04788 and 0.04778 Volt. Stabilisation had begun already during electrolysis.

14. In order to determine whether α-cadmium is formed during electrolysis if, this modification is present on the spirals before electrolysis begins, we shunted the cells 6 and 7 in a current of 1 milliampère. In this way we deposited upon the α-cadmium which was present, a fresh quantity of 30 mgr.

After formation we put a fresh (12.5 percent) amalgam into the cell, while a fresh solution of cadmium sulphate was also introduced.

Subsequent to this treatment the E.M.F. at 25°.0 C. was again 0.05026 Volt which proves that γ-cadmium had been formed on the old layer of α-cadmium.

15. On continuing our experiments we found that on one occasion

[1]) Trans. Amer. Electrochem Soc. **15**, 435 (1909).

cells of 0.047 Volt E.M.F, on another, cells of 0.050 Volt E.MF. were obtained.

As our dilatometric measurements had shown that stabilisation occurs with great velocity at 50°, we prepared cells (C and O) at 47°.9. The dilute amalgam was then taken out and an 8.5 percent (by weight) amalgam was put in, while a fresh solution of cadmium sulphate was used. We substituted an 8.5 per cent amalgam for a 12.5 percent as our intention was to measure these cells also at 0° C.; At this temperature the 12.5 percent amalgam is a monophase system and such a system must not be used.

In this way we found at 25°.0 C.

Cell C: 0.04745 Volt.
Cell O: 0.05022 „

The cadmium in cell C had thus been stabilised at 47°.9.

16. In order to check the results found up to this point we also determined the E. M. F. of our stable and metastable cells at 0° C. If the differences in E. M. F. at 25°.0 between the different cells were really to be ascribed to the presence of α-cadmium (cell C) and γ-cadmium (cell O) the difference which was at 25°.0 C. 2.8 millivolt ought to increase at 0° C. as we are at that temperature at a greater distance from the metastable transition point α-cadmium $\rightleftarrows$ γ-cadmium.

The measurements at 0° C. gave the following results:

cell C: 0.05225 Volt.
cell O: 0.05626 „

While the difference was **2.8** millivolt at 25°.0 C. it has increased as might be expected to **4.0** millivolt at 0° C.

17. Several phenomena which are described by HULETT, but which are obscure until now may find an explanation in the light of our experiments. HULETT says: "A number of cells were made with addition of $Cd(OH)_2$ thinking this might make a more uniform cadmium deposit; also the air was completely removed from three before sealing, and in others the air was removed and the cell saturated with nitrogen and with hydrogen. All of these gave very variable results, but in each case only 10 milligrams of cadmium had been deposited on the spiral, and I have lately learned this is too little cadmium, since some cells prepared as above described, excepting that only 10 mg. of cadmium was deposited on each spiral, showed the same irregularities and tendency to constantly decreasing electromotive force. These cells were recently all discharged and then reversing

the current about 26 mg. of cadmium was deposited on each platinum spiral, and they seem to be all coming together nicely and to the value indicated by the old cells".

18. Our observations agree perfectly with those of HULETT but we have to add the following restrictions: A number of our cells in which only 10 mgrs. of cadmium were deposited indicated immediately after formation an E. M. F, of 0.0502 Volt at 25°.0 which *decreased* during 2 days. Then it became constant: 0.047 Volt. Transformation into α-cadmium had consequently occurred; the fact that only a small quantity of cadmium is present causes the E. M. F. to reach very soon its definite lowest value. The phenomenon observed by HULETT is therefore the quick stabilisation of γ-cadmium.

19. Prof. HULETT has been kind enough to communicate to us the following facts: "Twelve cells which had been sealed after formation remained unchanged from March 18th 1905 to May 7th 1914, i. e. during 9 years. Their E. M. F. has been during all this time 0,0505 Volt. The quantity of cadmium on the spirals varies between **3.7** and **13.7** mgrs. of cadmium".

20. The decrease of E. M. F. which had been observed with cells which contain only 10 mgrs. of cadmium is consequently not to be ascribed to the minute quantity of metal [1]) deposited on the spirals; this quantity is much less in the cells which have been constant during 9 years. The reason of the decrease in E. M. F. of those cells is the transformation of γ-cadmium into α-cadmium.

21. In order to check this conclusion we prepared a number of cells (at room temperature) which only contained 5 mgrs. of cadmium on the spirals. Some of these remained metastable (0.050 Volt) while others were transformed into the stable form (0.047 Volt) after some days.

22. Although the discussion of a number of questions must be delayed until a subsequent paper, we will mention here the behaviour of cadmium which has not been formed by electrolysis.

In our second paper we stated that a piece of cadmium chosen at random which had been produced from the molten metal contains three modifications: α, β and γ-cadmium. If such is the case, it might

[1]) OBERBECK found [Wied. Ann. **31**, 337 (1887)] that a layer of metal A of 2×10^{-6} mm. suffices to give to a metal on which it has been deposited the potential of A. As the surface of the spirals in the H. C. was 0,28 cm^2 the layer of cadmium deposited is much thicker.

be expected that the potential of such a material against cadmium which has been formed by electrolysis should be zero. In order to test this conclusion we carried out the following experiment: We prepared a certain quantity of electrolytic cadmium (Prep. *A*) (Comp. our second paper § 8) and determined (at 40°) the potential difference between this material in a solution of cadmium sulphate which was half-saturated at 15° C. and:

1. Cadmium, which we received from KAHLBAUM (molten) in a finely divided state (Prep. B).

2. Cadmium which we had used in our dilatometric measurements; in this material the presence of γ-cadmium was presumed. (Prep. C).

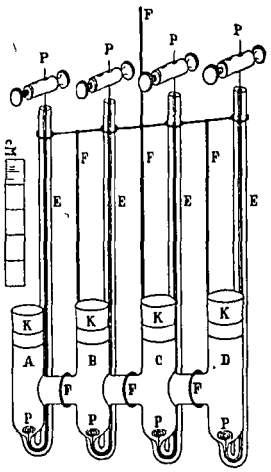

Fig. 3.

Making use of the small apparatus shown in Fig. 3 we first determined the potential difference between two samples of the same material, subsequently that between samples of different preparations. In this way we found:

E. M. K. of A against A = 0.000037 Volt.
„ B „ B = 0.000018 Volt.
„ C „ C = 0.00000 Volt.
E. M. K. „ A „ B = 0.000037 Volt.
„ A „ C = 0.000037 Volt.

From these measurements we see that γ-cadmium is really present in our preparations, as the dilatometer had shown.

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

(July 3, 1914).