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## KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

## PROCEEDINGS OF THE MEETING

of Saturday May 25, 1901.

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The following papers were read:

**Chemistry.** — Professor H. W. BAKHUIS ROOZEBOOM presents a communication on "Cadmium amalgams."

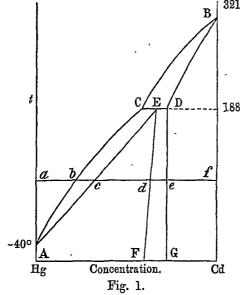
The desirability of the investigation of the nature of the cadmium amalgams arises from the use of these amalgams in the WESTON-cell. The discussion <sup>1</sup>) about the irregularities occurring when using this cell could not lead to a satisfactory conclusion until a better insight

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1) Compare Proceedings of June 30 and Oct. 27 1900 and Febr. 23 1901.

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was obtained into the nature of these amalgams. Mr. BIJL has now brought this investigation to a provisional conclusion and obtained the following results.



<sup>321</sup> Cadmium and mercury are miscible in all proportions when in a liquid state at a sufficiently high temperature. From these fused mixtures crystals are depos-188° ited on cooling which are represented in Fig. 1 by the two curves A C and C B. The first runs from  $A = -40^\circ$ , the melting point of mercury, to  $C=188^\circ$ ; the second from this point to  $B=321^\circ$ , the melting point of cadmium. The two curves meet at C forming an angle. Both the curves which have been determined

by the thermometric and by the dilatometric method, indicate the points at which solidifications begins.

None of the liquid amalgams, however, solidify completely at a constant temperature; solidification always takes place through a larger or smaller range of temperatures. The end of this could not be sharply defined thermometrically, but on the other hand the commencement of the fusion of the amalgams which had become solidified by sufficient cooling could be determined dilatometrically.

In this manner the lines A E, E D and D B were obtained as final solidifying, or commencing melting points. From this it appears that the whole solidifying figure belongs to the type of one of the cases which I have formerly distinguished in the systems of two substances which on solidifying yield exclusively mixed crystals.

The lines AE and DB represent the two possible series of mixed crystals. At 188° they follow each other with a comparatively small hiatus between E and D, which points correspond approximately with 75 and 77 atoms of cadmium per 100 atoms of the mixture.

The following change must therefore take place when heat is added at 188°:

mixed crystals  $E \rightarrow$  liquid C + mixed crystals D

and the reverse on withdrawing heat.

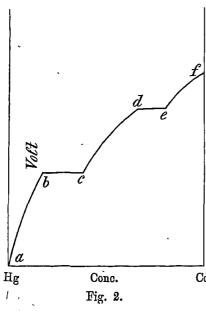
As the point C is situated at 67 percent, all the amalgams below

67 percent Cd. solidify to homogeneous mixed crystals of the mercury type. Similarly all amalgams over 77 percent of cadmium solidify to homogeneous mixed crystals of the cadmium type. The behaviour of the 67-77 percent amalgams is more complicated. These all begin by depositing crystals of the Cadmium type up to 188°. The change:

liquid C + mixed crystals  $D \rightarrow$  mixed crystals E',

then takes place so that 67-75 percent amalgams (at the left of E) are converted into mixed crystals E + liquid C and solidify on further cooling\_to mixed crystals of the mercury type; on the other hand the .75-77 percent amalgams completely solidify at 188° to a conglomerate of the crystals E and D of both types.

The very important question in how far the limits of these two series of mixed crystals, which exist together at 188°, change



as the temperature falls, has been studied electrically. A change in the composition of such limiting mixed crystals appears as a rule to take place but very gradually, so that it was now, as in former instances, not possible to prove its existence by thermometric or dilatometric means. With this metallic mixture however,

the opportunity presented itself of studying the matter by electrical methods. At the same time all the other percentages were investigated in order to obtain a first instance in Cd which the electrical conduct of a metal-

lic alloy was known for all its various proportions.

The EMF of alloys of every degree of concentration was measured in a solution of cadmium sulphate with a reversible mercury electrode as positive pole at temperatures of  $25^{\circ}$ —75°.

If we draw, in fig. 1, a horizontal line for instance at  $25^{\circ}$  it will intersect the different areas in such a manner that all the amalgams from a to b are liquid and therefore, form only one phase. From b to c they consist of the heterogeneous system consisting of the liquid phase b and of the solid phase c which consists of mixed crystals. From c to d every percentage is  $\tilde{a}$ -homogeneous mixed crystal.

If we assume that the limiting representatives of the mixed crystals

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which can exist together at 188°, are situated at lower temperatures on the lines EF and DG, we then have at 25° d and e-as limits and all the percentages between these are again heterogeneous and consists of both the mixed crystals d and e. On the other hand we have again from e-f a series of homogeneous mixed crystals ending with pure cadmium.

The line indicated in fig. 2 shows the EMF of the cells described in which the negative pole consists of the whole series of the amalgams in succession. The letters correspond with those in fig. 1. It therefore appears, that as long as we are dealing with a series of amalgams consisting of one phase (ab, cd, ef) whether liquid (ab)or solid (cd and ef) the E. M F varies regularly with the concentration of the amalgam. On the other hand we have in two cases a constant E M F accompanying variable concentration, namely from b to c and from d to e. In the first case it corresponds with the fact that the amalgam is a two-phased one (liquid b and solid c): in the second it must, therefore be also two-phased, but both phases are now solid mixed crystals (d and e). In this manner the limits of the horizontal part d e could be determined for different temperatures. From this it was found that on cooling below 188° the limits diverge still further until at 25° they have become: 65 and 80 atoms of cadmium percent.

The horizontal line bc is of great significance for the WESTONcells. We can now see plainly why a cell of constant EMF may be easily constructed if only the percentage of the amalgam which serves as negative pole is chosen somewhere on this line. We then have an amalgam which is partly liquid and partly solid. Such a mass usually attains equilibrium quickly and sharply when the temperature is changed. Moreover, the composition of the alloy remains on the line for a considerable time even though the total amount of cadmium decreases by the action of the current. This merely causes a slight diminution in the amount of mixed crystals and an increase in the volume of the liquid but the composition of both and consequently the EMF remains constant.

The extremities of the line bc alter, however, their position with the temperature as shown in fig. 1. This was noticed most plainly when determining the EMF: the positions of the points b and cthus found correspond exactly with those in fig. 1.

The many irregularities which have been observed when using WESTON-cells may be easily explained by the fact that up to the present an amalgam has been used containing too large a proportion of cadmium, too near to point c, so that on cooling one soon got outside

of the horizontal part, or in other words solid mixed crystals were obtained, the E M F of which was different from that of an amalgam represented by the horizontal line and which reached equilibrium much less rapidly than the semi-liquid amalgams.

Microbiology. — "Further Researches concerning Oligonitrophilous Microbes." By Prof. M. W. BEIJERINCK.

In my first paper on oligonitrophilous microbes  $^{1}$ ) I still left the question unanswered after the forms which develop in the light, in nutrient liquids, which only contain traces of nitrogen compounds, and whose nutrition with carbon can only be effected from the carbonic acid of the air.

The experiments to answer this question were made as follows. Large flasks were plugged with cotton wool or filtering paper, so that the air has free access, or closed in such a way that the air could be renewed, and that, at each renewing, it must pass through strong sulphuric acid in order to be deprived of the nitrogencompounds. These flasks had been half filled with

> 100 Tap- or distilled water 0.02 K<sup>2</sup> H PO<sup>4</sup>

and infected with a not too slight quantity of garden-soil, e.g. 1 to 2 grs. per liter  $^{2}$ ).

They were placed in winter at a window on the south, in spring and in summer on the north-west, and in the beginning they were now and then shaken, in order to sink the floating film of calciumphosphate, which forms at the surface.

As the rate of nitrogen and carbon compounds is too slight to cause any appreciable development of colourless microbes, no further cloudiness results, but that of the easily precipitating phosphate. But in winter after six to eight, in summer after four to five weeks, a characteristic flora develops consisting of some species

<sup>1)</sup> These Proceedings of March 30, 1901.

<sup>&</sup>lt;sup>2</sup>) The Delft tap-water contains at present 0.42 mG. nitrogen per L., the gardensoil used 0.56 pCt. nitrogen (analyses of Mr. A. v. DELDEN); but this nitrogen can only for a minimal portion (as ammonia and nitrate-nitrogen) be assimilated by microbes. The oligonitrophili themselves possess the specific faculty of feeding on the nitrogen from the atmosphere.