KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN TE AMSTERDAM.

PROCEEDINGS OF THE MEETING

of Saturday December 27, 1902.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige Afdeeling van Zaterdag 27 December 1902, Dl. XI).

CONTENTS.

The following papers were read:

Chemistry. — "*Tin amalgams*". By Prof. H. W. BAKHUIS ROOZEBOOM.

(Communicated in the meeting of November 29, 1902).

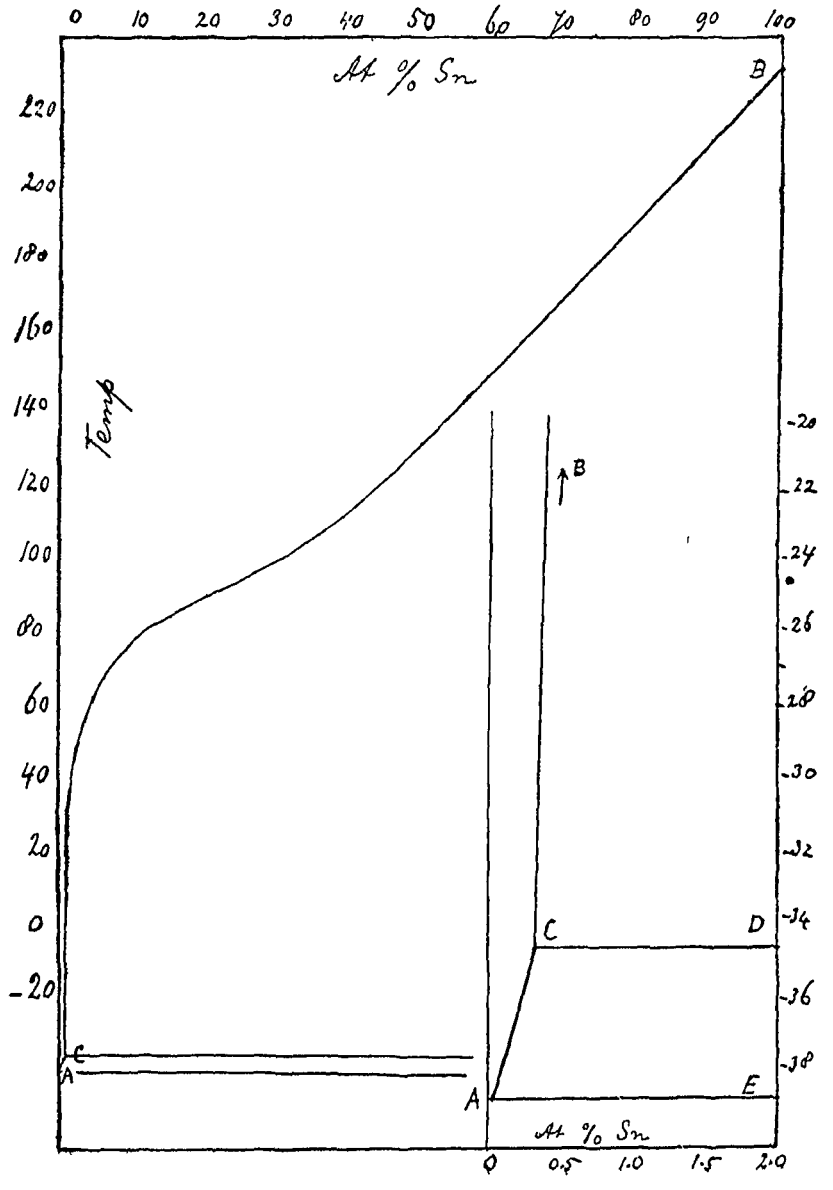
As the number of properly studied amalgams is still very small I directed Dr. VAN HETEREN to conduct an investigation on tin amalgams in connection with the research on cadmium amalgams by Dr. BIJL. The more important results are communicated here.

In the liquid condition tin and mercury are miscible in all proportions. From the different mixtures a solid phase is deposited at different temperatures. The points at which solidification begins are indicated in the accompanying figure by two lines AC and CB

which meet each other at C (0.3 at. % Sn and $-34°.5$) in a sharp angle.

As the line CB ends in the melting point of tin, the solid phase which deposits on cooling must be either tin or mixed crystals in which ordinary tin occurs as a component. On analysis, the solid phase which has separated from the liquid amalgam at 25° was found to be composed of 94 atom % Sn.

On account of the difficulty of obtaining trustworthy results in,



LINE *BC*.

At. % Sn.	Temp.	At. % Sn.	Temp.
100	231°.6	20.37	90°.0
89 95	211 .6	10.79	79 .7
76.62	183 .7	5.17	65 .2
61.44	155 .2	1.20	25 .0
49.99	133 .4	0.60	0 .0
35.33	107 .4	0.36	—18.8
28.96	99 .0	0.30	—34.5

this manner, measurements of the *E. M. F.* were also made at 25° of amalgams of 0.001—100 atom % Sn against an amalgam of 16 atom %.

These measurements led to the results that the unsaturated amalgams have a *E. M. F.* rising with the amount of tin until at 1.2 atom % saturation sets in. From this concentration up to 99 atom % the potential remains unchanged, consequently two phases of unchangeable concentration must exist between these limits; one of these is the liquid one of 1.2 %, the other the solid one containing 99 atom %.

At 25° the crystals deposited therefore consist of nearly pure tin which is the case in a still greater degree at higher temperatures. By a comparison of the values of the *E. M. F.* for amalgams of which the whole mass was liquid at 25° and 50° the heat of amalgamation could be calculated. The introduction of 1 gram-atom of Sn into a liquid amalgam with 0.01—1.00 atom % Sn, therefore nearly pure Hg, absorbs about 3000 calories.

The line *CB* may also be considered as the line of the solutions saturated with Sn. It takes a very peculiar course. The part from 120° up to the melting point of tin is nearly straight, the centre part shows a very rapid increase of the solubility with the temperature, the lower part, however, an exceedingly small increase and also an exceedingly small solubility so that the line approaches very closely the Hg-axis. In the lower part of the figure (p. 374) this part with its course towards the melting point of Hg has been drawn on a larger scale.

The extraordinarily great curvature of the central part of the line would lead to the supposition that the liquid mixtures of Sn + Hg in the absence of a solid phase would on further cooling separate into two layers.

On cooling below —34.5° a change takes place in all amalgams from 0.3 to 85 %, accompanied by a decided evolution of heat and decrease of volume. With increasing concentrations of Sn it first increases but then decreases in intensity. The maximum lies near 50 %. This change occurs in the figure on the line *CD* which therefore runs to at least 85 %.

The change causes a new phase to appear which also belongs to the second solidifying-line *CA*. The maximum in the intensity of the change on *CD* at about 50 % would lead us to suppose that mixed crystals having about this composition are formed. The modification of tin therein contained must differ from ordinary tin.

Between —34°.5 and —38°.5 these mixed crystals continue to be deposited from the mother-liquor (which moves along the line *CA*), this is accompanied by expansion. This change in volume diminishes as the amount of tin present increases and dies out near 75 %. The solidification point of pure mercury and also the final solidification point of all amalgams containing up to about 60 % Sn, lies at —38°.6 (line *AE*). As the line *CA* of the saturated solutions also ends here it would seem that at the solidifying point of Hg, the solubility of tin has decreased to 0, so that instead of a eutectic mixture only the remaining mercury solidifies.

Still, the point *A* bears quite the characteristic of a eutectic point as not only the line *AE* is horizontal, but all mixtures up to 60 % Sn also remain a shorter or longer time at this temperature which proves that a residual liquid is solidifying completely.

A great uncertainty still exists as to the nature of the tin-modification which occurs in mixed crystals below —34°.5 chiefly because it has so far not been possible to discover the part played in the amalgams by the grey modification of tin which may occur below 20° C.

But from the change in volume which takes place in the different transformations at and below —34°.5 we may argue that the specific volume of the tin must be smaller than that of the grey modification and larger than that of liquid and, therefore, also of ordinary tin.