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**Physics.** "*The system tin*". By Prof. A. SMITS and Dr. H. L. DE LEEUW.  
(Communicated by Prof. A. F. HOLLEMAN).

(Communicated of the meeting of October 26, 1912).

As is known when molten tin is cooled down, the tetragonal modification deposits under ordinary circumstances, which form was first described by MILLER<sup>1)</sup> in 1843. This form shows a point of transition at 18°), below which the gray tin is the stable modification.

In the years 1880 and 1881 TRECHMANN<sup>2)</sup> and FOULLON<sup>3)</sup> discovered moreover a third modification, viz. a rhombic one, which can be formed when molten tin is exceedingly slowly cooled down, and which is *brittle*.

It was now natural to assume that this form of tin forms at higher temperature from the tetragonal modification, for it had been known for a long time that tin heated to about 200° becomes *brittle*, and that in England this circumstance has been profitably used to obtain the so-called *corn tin* or *grain tin*. In this process tin is heated to some degrees under the melting-point, after which it is dropped from a great height on a stone plate, on which the metal breaks up into pieces resembling basalt. The above-mentioned supposition was further supported by observations by KALISCHER<sup>4)</sup>, in which it appeared that when tin is heated to about 200°, the aspect changes, and the metal assumes the appearance of *moiré métallique*.

As SCHAUM<sup>5)</sup> already observed these experimental data make the existence of a point of transition at about 200° very probable, and as the spec. gravity of the tetragonal and rhombic modification, which amount to 7,25 resp. 6,55 at 15° differ pretty much, it seemed the natural course to take to try and find this point of transition by a dilatometrical way. COHEN and GOLDSCHMIDT's<sup>6)</sup> experiments with an oil-dilatometer, however, (in which no difficulty was experienced from any generation of gas) did not furnish the least indication for the existence of a point of transition, for the expansion, represented as function of the temperature, appeared to be a perfectly straight line from 175° to 210°. Though these experiments had yielded a negative result, already a year before WERIGIN, LEWKOJEFF and TAMMANN<sup>7)</sup> had

1) Phil. Mag. (3) 22, 263 (1834).

2) COHEN-VAN EYK, Z. f. phys. Chem.

3) The mineralogical magazine and Journal of the Mining Soc. 3, 186 (1880).

4) Verh. der k. k. geologischen Reichsanstalt 1881, 237.

Jahrb. der k. k. geologischen Reichsanstalt 1884, 367.

5) B.B. 15, 722 (1113).

6) Lieb. Ann. 308, 18 (1899).

7) Z. f. phys. chem. 50, (1904).

8) Drud. Ann. 10. 647 (1903).

found indications which seemed to point to a point of transition in the neighbourhood of  $200^{\circ}$  in a determination of the velocity of effluxion of some metals, among which tin, at different temperatures.

Their results were the following :

temperature	velocity of effluxion
162.8	$0.6 \pm 0.3$
173.4	$1.7 \pm 0.3$
183.8	$3.9 \pm 0$
193.5	$8.2 \pm 0.1$
203.8	$12.1 \pm 2.1$
204.0	$3.2 \pm 0.3$
214.8	$4.1 \pm 0.5$
224.6	$10.5 \pm 0.4$
235.7	112.3

The above-mentioned investigators make the following remarks about this result :

“Von Interesse sind noch die beim *Zinn* bei  $200^{\circ}$  deutlich auftretenden Abnormalitäten in der Temperaturabhängigkeit der Ausflussgeschwindigkeiten. Beim *Zinn* fällt bei jener Temperatur plötzlich die Ausflussgeschwindigkeit. Der Grund hierfür kann nur in der Bildung einer neuen Kristallart, also im Auftreten eines Umwandlungspunktes gesucht werden. Von *Zinn* ist bekannt, dass es bei  $200^{\circ}$  spröde und pulverisierbar wird. Genauer sind diese Umwandlungspunkte bisher nicht untersucht worden.”

Why in reference to these experiments COHEN and GOLDSCHMIDT give  $195^{\circ}$  for the point of transition in question in the “*Chemisch Weekblad*”, and  $170^{\circ}$  in the *Zeitschr. f. phys. chem.* is quite unaccountable. Their assertion : “Bringt man die in Tabelle 4 (the above table) gefundenen Werte in Zeichnung, so entstehen zwei Kurven, welche sich bei etwa  $170^{\circ}$  schneiden, somit auf einen Umwandlungspunkt bei dieser Temperatur hinweisen”, is decidedly erroneous, and proves that they have not understood the significance of this curve.

In view of the fact that the experiments on the velocity of effluxion render a point of transition at more than  $200^{\circ}$  very probable, it was very desirable to get certainty on this point by another way, the more so as the experiments about the velocity of effluxion refer

to pressures of 500 kg. per cm<sup>2</sup>. There was therefore every reason to rejoice that Mr. DEGENS, when revising his Thesis for the Doctorate: "Legeeringen van tin en lood" (Alloys of tin and lead) wanted to make another attempt to find the expected transition between tetragonal and rhombic tin in a dilatometric way, though his predecessors had only obtained negative results.

As Mr. DEGENS found it impossible to obtain reliable results with paraffin oil, which had been used as dilatometric liquid by COHEN and GOLDSCHMIDT, in consequence of the generation of gas, however slight, one of us (SMITS) advised Mr. DEGENS to use an air-dilatometer with a twice bent capillary. To prevent any injurious decomposition of the dilatometric liquid, mercury was used by Mr. DEGENS, to include the air in the dilatometer, although in this way there was, of course, a possibility that during the experiment, especially when it had to be continued for a long time, appreciable quantities of gaseous mercury could be absorbed by the tin. Mr. DEGENS, however, expressly states that "it was never observed that the metal was attacked by mercury vapours".

By the aid of this air-dilatometer Mr. DEGENS really found an indication about the existence of a point of transition, viz. at 161°.

Since we have been occupied with the tin-problem, we have begun to mistrust this temperature, because different phenomena led us to expect a point of transition at  $\pm 200^\circ$ . And as it seemed very desirable in connection with the already partially published investigation about the system tin, to know the exact situation of the point of transition between tetragonal and rhombic tin, an investigation was undertaken also by us to determine this point dilatometrically.

When we repeated Mr. DEGENS' experiments we found first of all that by this way of procedure a point of transition can really be demonstrated, but that in successive experiments this point of transition descended. This pointed to an absorption of gaseous mercury by the tin during the experiment. On investigation of the tin used it appeared clearly that the tin contained appreciable quantities of mercury, which to our great regret condemned Mr. DEGENS' method. We regretted deeply that we had to come to this conclusion, particularly because Dr. DEGENS was known to one of us (SMITS) as a man full of enthusiasm for his work, who carried out his investigations with great experimental skill, in the conviction of having left no means untried to test the validity of his results. In this case, however, he has been mistaken.

In order to take the experiment in such a way that the results

obtained were entirely reliable, we turned back to the ordinary dilatometer, and tried to attain by means of the oil of the vacuum pump of GÖRDE, which seemed to be very suitable as dilatometric liquid, that no generation of gas took place at temperatures up to the melting-point of tin. By thoroughly boiling the oil in the vacuum of the pump, by then allowing it to flow into the dilatometer vessel, and afterwards heating the whole  $20^\circ$  above the melting-point of tin we managed to prevent any generation of gas even above the melting-point of tin <sup>1)</sup>.

With the dilatometer filled in this way curves of expansion and of contraction were determined as accurately as possible by putting the apparatus in a thermostat with oil resp. a molten mixture of  $\text{KNO}_3$  and  $\text{NaNO}_2$ , by raising the temperature every time  $10^\circ$ , resp. lowering it, and by then reading the position of the oil level after 15 minutes. Though the obtained lines have not appeared to be perfectly straight, as COHEN and GOLDSCHMIDT found, yet no indication of a point of transition was to be detected. As according to Mr. DEGENS' method, by the same procedure a point of transition *was* found for tin containing mercury the mercury seemed to be a positive catalyst for the conversion in the point of transition. In connection with this we proceeded to the determination of the transition point of tin to which small quantities of mercury had been added.

In this it was not only found that for every mixture very clearly a transition point occurred, but also that the transition point was greatly lowered by mercury, which is in accordance with the slight heat of transition.

We found :

	at. % Hg of the mixture	transition temperature
1	0.12	$173^\circ$
2	0.22	$151^\circ$
3	0.34	$133^\circ$
4	0.49	$133^\circ$

The third and fourth determinations point to the existence of three-phase equilibrium, which is also in harmony with this that the transition

<sup>1)</sup> Not to lose the oil during the heating up to this high temperature, the upper end of the capillary was provided with a wider vessel.

points 3 and 4 do not lie on the line drawn through 1 and 2<sup>1)</sup>.

If we use the first two observations to extrapolate to the composition 0 atom % Hg, which is, of course, a rather inaccurate method, we find 200°,5 for the transition point of pure tin.

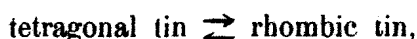
At all events it appeared from this that the transition point of pure tin must lie in the neighbourhood of 200°, and as it had appeared from the preceding experiments that the conversion in the transition points of mixtures containing Hg is attended with a distinct though small diminution of volume, it must also be possible to find the transition point for perfectly pure tin by dilatometrical way.

It was clear that the conversion in pure tin proceeds slowly, and that at every temperature we should have to wait long to attain reliable results.

When the thermostat, in which the dilatometer which contained 250 gr. of tin, was placed, was first regulated at 240°, so that the tin melted, and when then comparatively rapidly the thermostat was brought to 190°, it appeared that after the dilatometer had assumed the temperature of 190°, no change of volume worth mentioning took place even after 24 hours, from which it was inferred that on solidification exclusively the tetragonal modification had been formed, and that therefore the tin had solidified at the metastable point of solidification.

In agreement with this experiment it appeared that when the bath was regulated at 206°, and also the tin had assumed this temperature, an increase of volume took place, which could not practically be considered as completed until after 48 hours. If then the thermostat was again put at 190°, a diminution of the volume set in again at constant temperature.

This phenomenon, which points to the conversion :



shed a great deal of light on the fact of tin becoming brittle at about 200°, on the preparation of corn tin, and also on KAISCHER's observation, particularly because it is very probable that the above conversion proceeds most slowly in pure material.

It further appeared from these experiments, just as from those made with tin containing mercury, that the difference in specific gravity between the tetragonal and the rhombic modification is much smaller at  $\pm 200^\circ$  than at the ordinary temperature, as the variation of volume found, which, it is true, had probably not yet reached its

<sup>1)</sup> This investigation is being continued to get to know more about the system tin-mercury.

maximum value, amounted only to about 0,3 cm<sup>3</sup>., which variation of volume corresponded with a displacement of the oil-level of  $\pm 6$  cm. in the capillary.

With a purpose of determining the accurate situation of the transition point the experiments described above were repeated several times, which resulted in a final determination of the transition point, which had been sought so long in vain, at  $\pm 202,8^\circ$ , for at this temperature no variation of volume had taken place even after four days, whereas below it a diminution of volume and above it an increase of volume was observed. The inaccurate extrapolation which was mentioned before, and which gave  $200,5^\circ$  for the transition temperature, yielded, therefore, a result which was pretty near the truth.

As we have always got the impression in this investigation that even on slow cooling of pure liquid tin exclusively or almost exclusively the tetragonal modification, which is metastable above  $203^\circ$ , is formed, and that even with pretty slow heating of the tetragonal form the conversion to the rhombic modification fails to appear, it seemed pretty certain that only the metastable unary melting-point of tin was known. To find the stable unary melting-point the curve of heating was determined of tin which had been heated for 48 hours at  $220^\circ$  in a thermostat. The result yielded by this investigation and the particularities of the pseudo system derived from it will be communicated in a following paper.

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**Chemistry.** — "*The phenomenon of double melting for fats*". By Prof. A. SMITS and S. C. BOKHORST. (Communicated by Prof. A. F. HOLLEMAN).

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GUTH<sup>1)</sup>, who has been extensively occupied with the preparation of simple and mixed glycerin esters of fatty acids, has observed the phenomenon of *double melting* for several of these fats. Thus we hear about tristearin that the crystallised tristearin has only one melting-point at  $71^\circ.5$ , whereas the tristearin that has first been melted, then cooled in a capillary, and then solidified, first melts at  $55^\circ$  on supply of heat, then solidifies again, and then melts again at  $71^\circ.5$  on further supply of heat. On the ground of these phenomena GUTH has come to the result that the melted and rapidly

<sup>1)</sup> Z. f. Biol. 44, 78 (1902).