

Citation:

S.C. Bokhorst & A. Smits, The phenomenon of double melting for fats, in:
KNAW, Proceedings, 15 I, 1912, 1912, pp. 681-683

maximum value, amounted only to about 0,3 cm³., which variation of volume corresponded with a displacement of the oil-level of ± 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° , 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° 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.

Anorg. laboratorium of the University.

Amsterdam, Oct. 23, 1912.

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

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

GUTH¹⁾, 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° 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

¹⁾ Z. f. Biol. 44, 78 (1902).

cooled mass has not yet crystallised, and is therefore in a glassy metastable state. On supply of heat the metastable state would pass into the stable one, in which so much heat is liberated that small quantities are thereby completely melted, which later solidify again, but which melt again when the melting point has been reached for the second time on supply of heat.

KREIS and HAFNER¹⁾ have repeated GUTH's experiments and found them perfectly confirmed, but what rouses our great astonishment is this that they entirely concur in GUTH's view of the matter.

Without entering into GUTH's explanation, which is, putting it mildly, very improbable, we will state here very briefly what has been the result of an investigation which we have carried out with the purest *tristearin* of KAHLBAUM.

It is clear from what precedes that in GUTH's opinion the temperature of 55° cannot be called a melting point of *tristearin*. Our experiment, however, has shown that GUTH has stated the truth, in spite of himself, and that we have, indeed, to do here with two melting-points. It has namely appeared that the observed peculiar phenomenon is caused by the existence of two different crystallised modifications of *tristearin*, of which the metastable one appears most readily. The velocity of crystallisation of the stable form is still very small, even a few degrees below the point of solidification of the metastable form, and much smaller than that of the metastable modification. Hence when the liquid is cooled down to below the point of solidification of the metastable form, the latter is always made to crystallise.

If the liquid is kept for some time at a temperature between the two melting-points, the stable form crystallises, but with a very slight velocity.

If we start from the metastable modification obtained by comparatively rapid cooling of the liquid, and if this metastable modification is placed in a bath the temperature of which rises slowly, the metastable unary melting-point appears at $54^{\circ}.5$; if the temperature of the bath is carried up to 63° , and if this temperature is kept constant for some time, crystallisation sets in slowly, and only after 2 or 3 hours everything has become solid and has passed into the stable modification. If the temperature of the bath is made to rise still further, the stable unary melting point occurs at $70^{\circ}.8$. The phenomena described just now have also been studied under the microscope, in which our views were perfectly confirmed in all respects.

¹⁾ B. B. 36, 1123.

In conclusion we will still remark here that the system *tristearin*, which according to our investigation exhibits the phenomenon of *allotropy*, and is probably monotropic, has also furnished a confirmation for the theory of allotropy, as it has appeared here again that the *solid phases are states of internal equilibrium*. Particularly for the metastable modification it could be clearly demonstrated that the solid substance which has assumed equilibrium at lower temperature, melted already below the metastable unary melting-point in case of rapid heating.

Hence it follows from what precedes that we have to assume two kinds of molecules α and β for the system *tristearin*, and that the differences between the two crystallised states are owing to the difference in situation of the internal equilibria.

That the phenomenon of double melting observed for other fats, will have to be accounted for in the same way, is more than probable.

Anorg. Chem. Laboratory of the University.

Amsterdam, Oct. 25.

Chemistry. — “On the system ammonium sulphocyanate-thiourea-water.” By Prof. A. SMITS and A. KETTNER. (Communicated by Prof. A. F. HOLLEMAN).

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

A recently published paper by ATKINS and WERNER¹⁾ induces us briefly to communicate already now the results of an investigation which is not yet quite completed.

The pseudo binary system $\text{NH}_4\text{CNS} - \text{CS}(\text{NH}_2)_2$ was examined. The melting-point figure found for this system (fig. 1) pointed with great probability, to the existence of a compound $\text{NH}_4\text{CNS} \cdot 4 \text{CS}(\text{NH}_2)_2$, because the curves of cooling on the right of this concentration did not give a single indication for a eutectic point at $\pm 105^\circ$, whereas this *was* the case for mixtures on the leftside of this concentration. ATKINS and WERNER are, however of opinion that the compound $\text{NH}_4\text{CNS} \cdot 3 \text{CS}(\text{NH}_2)_2$, follows from the melting-point lines found by them, which show a close resemblance to ours²⁾.

To get perfect certainty about the existence of the compound 1 4,

¹⁾ Journ. Chem. Soc. 101, 1167 (1912).

²⁾ On account of the rapid conversion of $\text{CS}(\text{NH}_2)_2$ at high temperature, the mixtures with more than 70% $\text{CS}(\text{NH}_2)_2$ had to be investigated by Soehn's capillary method.