

*Citation:*

Kettner, A. & A. Smits, On the system ammonium sulphocyanate thiourem water, in:  
KNAW, Proceedings, 15 I, 1912, 1912, pp. 683-686

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  $\alpha$  and  $\beta$  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 WERNER <sup>1)</sup> 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 ours <sup>2)</sup>.

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

<sup>1)</sup> Journ. Chem. Soc. 101, 1167 (1912).

<sup>2)</sup> 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 SOCH's capillary method.

the study of the ternary system  $\text{NH}_4\text{CNS} - \text{CS}(\text{NH}_2)_2 - \text{H}_2\text{O}$  was taken in hand after the melting-point diagram had been determined, in which a method of analysis was worked out which enabled us

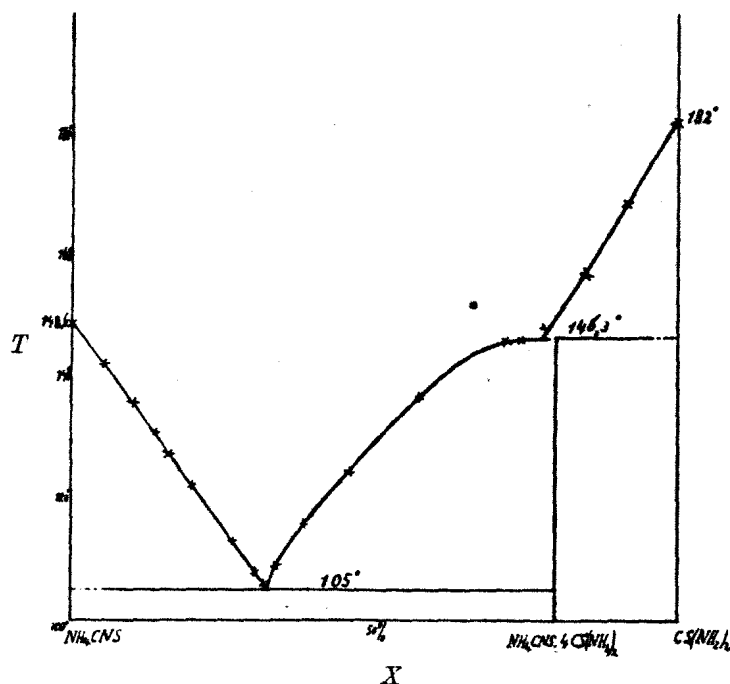


Fig. 1.

quantitatively to determine the ammonium sulpho-cyanate and the thiourea by the side of each other with sufficient accuracy.

The solubility-isotherms found at  $25^\circ$  and the investigation of the coexisting solid phases, in which the residu-method was applied for the determination of the binary compound (see fig. 2) afforded a proof for the validity of the conclusion drawn from the melting-point figure, so that the existence of the compound 1.4 may now be considered as conclusively proved.

Moreover the knowledge of the peculiar situation of the solubility isotherms led us to a simple explanation of the method of preparation of thiourea from ammonium sulphocyanate according to REYNOLDS and WERNER<sup>1)</sup>, which method had been unaccountable up to now.

The process of preparation is as follows: ammonium sulphocyanate is heated for some time up to  $160^\circ$ , then the liquid is poured into

<sup>1)</sup> Journal Chem. Soc. 83, 1 (1903).

cold water, and then the solid substance obtained by evaporation is recrystallised.

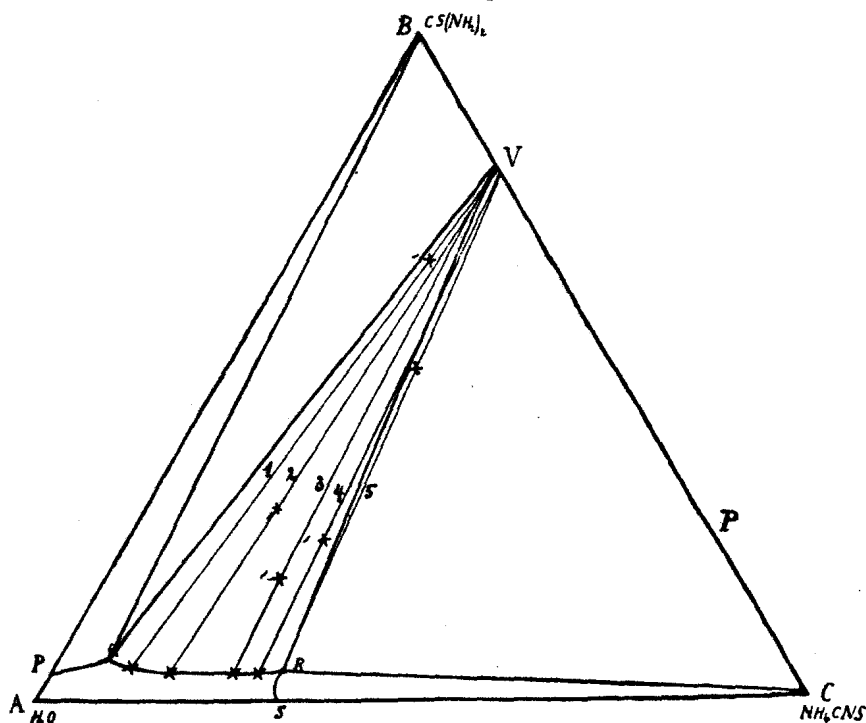


Fig. 2.

According to FINDLAY's<sup>1)</sup> experiments, and also according to ours the internal liquid equilibrium that sets in when ammonium sulphocyanate is heated up to  $160^{\circ}$  for some time, has the following composition 75%  $\text{NH}_4\text{CNS}$  and 25%  $\text{CS}(\text{NH}_2)_2$ . When the liquid is poured into cold water, this state is fixed. If we suppose that everything is solved at  $25^{\circ}$ , the obtained state lies in our figure on the line that joins the points  $P$  and  $A$ , and in the unsaturated region. If we now begin to make the liquid evaporate, the isotherm of the compound  $\text{NH}_4\text{CNS} \cdot 4\text{CS}(\text{NH}_2)_2$  will be passed, i. e. we may enter the region which is supersaturated of the compound 1,4 indicated by the point  $V$ , so that the latter deposits. If we now separate the solid substance from the mother liquor and if we solve the compound  $V$  in a new quantity of water, the obtained liquid will again lie in the unsaturated region, but now on the line that connects point  $V$  with  $A$ . This joining line accidentally does not cut the isotherm of the compound  $V$ , but that of the thiourea ( $B$ ), so that on evaporation of the solution, not the compound  $V$ , but thiourea will

<sup>1)</sup> Journal Chem. Soc. 85, 403 (1904).

deposit. It is clear that to obtain thiourea from the compound *V* it is not even necessary to dissolve the latter first entirely. It already suffices to bring the compound in contact with water, because the pure saturated solution of *V* is metastable, and will deposit thiourea specially on seeding with a crystal of this substance, which conversion continues till the compound has quite vanished.

With regard to the exact relation between the pseudo-binary and the unary *T*, x-figure of the system  $\text{NH}_4\text{NCS} - \text{CS}(\text{NH}_2)_2$ , we may state that it is being investigated, and that we hope that we shall soon be able to give it with perfect certainty.<sup>1)</sup>

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**Botary.** — “*On the demonstration of carotinoids in plants. Second communication: Behaviour of carotinoids with regard to reagents and solvents.*” By Prof. C. VAN WISSELINGH. (Communicated by Prof. J. W. MOLL).

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

The reagents by means of which coloration is brought about in carotinoids are the following: concentrated sulphuric, sulphurous and concentrated nitric acids, bromine water, concentrated hydrochloric acid with a little phenol or thymol, and iodine in potassium iodide or chloralhydrate solution. All these reagents cause blue coloration, except the iodine reagents which generally produce a green colour.

In this paper the use of sulphuric acid, bromine water and iodine in potassium iodide solution will be dealt with as well as two new reagents for carotinoids, namely, concentrated solutions of antimony trichloride and of zinc chloride both in 25 % hydrochloric acid. Solvents as well as reagents can also be successfully used in the microscopic investigation of carotinoids, and they also are dealt with in this paper.

#### *Sulphuric acid.*

T. TAMMES<sup>2)</sup> in her investigation of carotin used concentrated

<sup>1)</sup> This relation is probably pretty complicated, because different crystallized modifications exist of both pseudo-components. This was already known of  $\text{NH}_4\text{NCS}$ , but for  $\text{CS}(\text{NH}_2)_2$  it was revealed for the first time by this investigation.

<sup>2)</sup> T. TAMMES, Ueber die Verbreitung des Carotins im Pflanzenreiche, *Flora* 1900, 87. Bd. 2. Heft, p. 213.