

Citation:

A. Smits & Mooy, W.J. de, On the system chlorine - sulphurdioxyde, in:
KNAW, Proceedings, 13 I, 1910, Amsterdam, 1910, pp. 339-341

The investigation, which was carried out with a very sensible resistance thermometer, made by Messrs. DE LEEUW and ZERNIKE, yielded the results given in the table on p. 338.

These results enable us to draw also the T, X -section of the P, T, X -spacial figure corresponding to the pressure of 1 atmosphere in so far as the equilibria with solid phases are concerned or in other words the melting-point lines.

From the course of these melting-point lines (fig. 6), in which

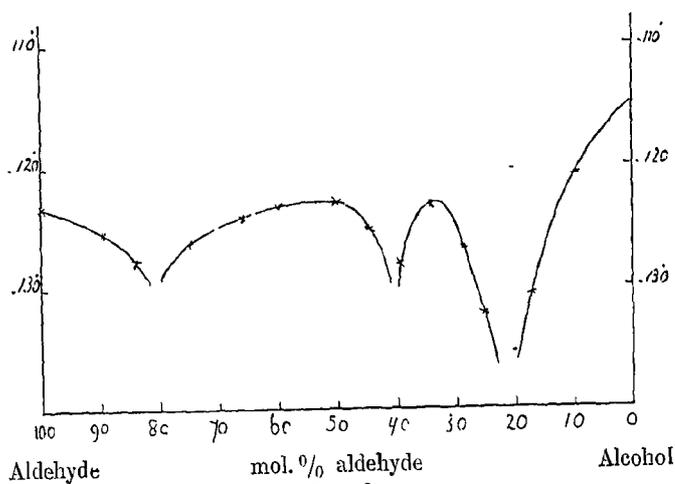


Fig. 6.

two maxima occur, one at 50 % and one at 33 % aldehyde, follows with sufficient certainty the existence of the two compounds $\text{CH}_3\text{COH.C}_2\text{H}_5\text{OH}$ and $\text{CH}_3\text{COH.2C}_2\text{H}_5\text{OH}$, which are considerably dissociated even at the low melting-point temperatures -122° and -123° .

Amsterdam, June 18. *Anorg. Chem. Lab. of the University.*

Chemistry. — “On the system chlorine-sulphur dioxide”. By Prof. A. SMITS and W. J. DE MOOY. (Communicated by Prof. A. F. HOLLMAN).

(Communicated in the meeting of June 25, 1910).

In our search for a clear example of the influence of light on heterogeneous equilibria we have fixed upon the above-mentioned system, of which it was already known that the conversions $\text{SO}_2 + \text{Cl}_2 \rightleftharpoons \text{SO}_2\text{Cl}_2$ do not take place in the dark and in the absence of a katalyser, while light or a katalyser as camphor, animal

carbon, etc. causes the equilibrium between sulphuryl-chloride and its dissociation products to set in comparatively quickly.

The purpose was first to study the T, X -figure corresponding to the pressure of 1 atm. in the dark and in the absence of a katalyser, and then take the same experiments in the light.

The investigation in the dark and in the absence of a katalyser is over now, and has yielded the result we anticipated, as appears from the subjoined figure, which only represents what has been found at and below the melting-point temperatures of the components, the determination of the boiling-point curves being postponed till afterwards.

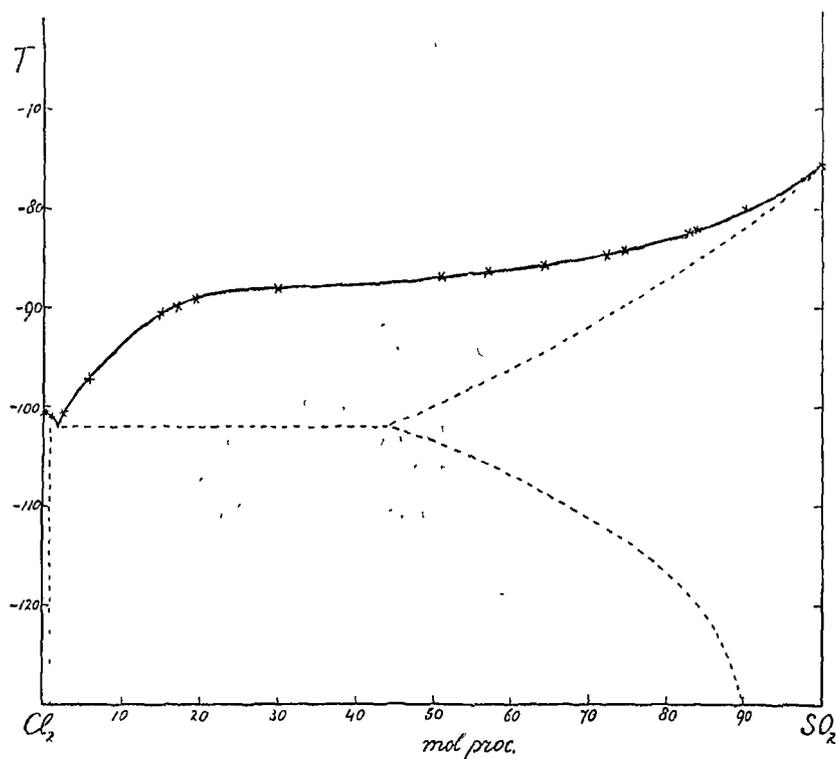


Fig. 1

The determinations, which were made with a very sensible resistance-thermometer, made after a device of Messrs DE LEEUW and ZERNIKE gave for the meltingpoint of Cl₂ the temperature of $-100^{\circ}.45$, and $-75^{\circ}.6$ for that of SO₂.

On addition of very small quantities of SO₂ to Cl₂ a lowering of

the end-melting-point was found, so this proved that the melting-point lines form a eutectic point.

It appeared that this eutectic point lay at $-102^{\circ}.3$ and at a concentration of about 1.5 mol.-% SO_2 .

As this eutectic point lies very near the Cl_2 -side, and so not very far below the melting-point of SO_2 , the shape of the melting-point line of SO_2 , which presents a distinct point of inflection is rather level, from which it appears at the same time that if the experiment is made in the dark, there is no question of the formation of a compound, which, however, is easy to verify after the experiment is finished. As is known, SO_2Cl_2 hardly dissolves in water, so that its presence is at once betrayed when the mixture is poured into water.

Further the diagram shows that mixed crystals very clearly appear. As it, however, appeared, that probably on account of the low temperature, the conversions may be easily retarded, the mixed crystal curves are dotted, because it is possible that when the experiments are repeated with baths of low temperature specially arranged for the purpose, small deviations will be found, though, of course; the type is fixed already now.

The experiment in the light, for which sunlight and also a quartz-mercury lamp was used, has already proved that rapid formation of sulfuryl-chloride takes place under these circumstances, in consequence of which the melting-point figure undergoes a considerable modification.

For the present we shall confine ourselves here to the statement that a mixture of 47.1 mol. % SO_2 , in which equilibrium had been established in sunlight, presented an initial point of solidification of about -80° , which point, therefore, lies considerably above the melting-point curve, as a proof that we have to deal here with another system.

What the shape will be of the whole T, X -figure of the system in equilibrium in the light, will be communicated on another occasion. We will investigate also the heterogeneous equilibria in the dark and in the presence of a katalyser, in which probably results will be obtained, deviating in some regards from those obtained in the light.

Amsterdam, June 22, 1910.

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