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H.R. Kruyt, The dynamic Allotropy of sulphur, in:
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with increase in volume, crystallisation will occur at an increased and solution at a reduced pressure. This is, moreover, in conformity with the change in pressure in the points R and R' along the saturation line under its own vapour pressure.

The same considerations as the above-cited may be also applied to the case when the substance F melts with decrease in volume.

(To be continued).

Chemistry. — “*The dynamic Allotropy of sulphur.*” (Fifth communication.)¹⁾ By Dr. H. R. KRUYT. (Communicated by Prof. P. VAN ROMBURGH.)

(Communicated in the meeting of January 25, 1913).

As point 5 of the résumé of my third paper on the above subject I wrote in 1909:

“Es wurden neue Untersuchungen über den Einfluss des S_{α} auf den Umwandlungspunkt $S_{rh} \rightleftharpoons S_{mon}$ in Aussicht gestellt”.

In connection therewith I wrote²⁾ in July 1911:

“Dr. VAN KLOOSTER of Groningen has this year started that investigation and although the provisional result is only of a qualitative character as yet it may be taken for granted . . .”

Nevertheless, Messrs. SMITS and DE LEEUW published, in these Proceedings (XIV, p. 461), an investigation concerning this question.

In the Zeitschr. f. Electrochemie³⁾ I communicated, in connection with some other questions regarding sulphur, that the above investigation had been continued and brought to a close, also to what conclusions it had led and that a detailed communication would soon appear; recently it appeared as the fourth communication in this series

Meanwhile, Dr. DE LEEUW (Proc. XV p. 584) has contradicted the above cited conclusions and condemned the still unpublished investigations in advance.

Although I should have every reason not to take any notice of that paper, two reasons in particular have induced me to repeat and extend

¹⁾ For the previous communications see Zeitschr. f. physik. Chem. viz. I: 64, 513 (1908); II: 65, 486 (1909); III: 67, 321 (1909) and IV: 81, 726 (1913).

²⁾ Chem. Weekbl. 8, 643 (1911).

³⁾ Z. f. Elektrochemie 18, 581 (1912).

the investigations of Dr. DE LEEUW and to communicate here the results. First of all, the criticism did not concern my work only, but also that of Messrs. VAN KLOOSTER and SMIT who carried this out at my request and whose work I wish to defend and in the second place, owing to a paper by Messrs. KOHNSTAMM and ORNSTEIN¹⁾, the question as to the change of the transition point of sulphur has been introduced into the discussion of the heat theorem of NERNST. Looking at the eminent importance of the problem whether the facts confirm or do not confirm the conclusions from the heat theorem, each experimental fact supporting the theorem must be as much as possible elucidated.

Therefore, I will discuss the said treatise of DE LEEUW, but only in so far as required by the considerations just mentioned.

I have first of all verified whether the result of DE LEEUW's experiment is correct namely, that a dilatometer, which contains a sulphur mixture rich in S_{μ} , after it has been placed for some hours in a thermostat at 70°—80° C., exhibits a rise of the liquid in the capillary which is followed by a fall. This indeed proved to be the case. This verification appeared to me necessary because the statements in DE LEEUW's table only contain observations of changes which sometimes amount to only $1\frac{1}{2}$ mm. and seldom more than 2 mm. For no one who has experience with the dilatometer these observations will have any definite value. And although the fact first investigated proved correct, the conclusions arrived at by DE LEEUW are not proof against a more elaborate investigation.

The rise observed is attributed in all the treatises cited to the change in volume in the conversion $S_{lh} \rightarrow S_{mon}$, because the conversions $S_{mon} \rightarrow S_{lh}$, $S_{\mu} \rightarrow S_{lh}$ and $S_{\mu} \rightarrow S_{non}$ take place with contraction of volume. Owing to the reaction $S_{\mu} \rightarrow S_{\lambda}$ taking place meanwhile, the S_{μ} concentration is attained at which the conversion $S_{lh} \rightarrow S_{mon}$ at the temperature of experiment ceases; hence the rise in the capillary ceases also and a fall is exhibited there as a consequence of the still proceeding reaction $S_{\mu} \rightarrow S_{\lambda}$. On elevation of the temperature the phenomenon ought to repeat itself each time. Such are the views of Dr. DE LEEUW. In fig. 1 the thin line with the arrows indicates the changes of condition which the sulphur in the dilatometer ought to pass through.

In my experiments, however, it appeared that the behaviour of the dilatometer is absolutely contrary to the expectations raised by this diagram.

¹⁾ These Proceedings XIV p. 802.



the dilatometer is not an instrument of precision not even when the best acting thermostat is used.

Below are given some of my investigations.

Table I contains the result of a series of experiments represented graphically in fig. 2. We notice that, when we wish to attribute the great rises at 76°.2 and 83°.0 to conversions according to the scheme of fig. 1 it becomes inexplicable why at the temperatures 86°.7 and 91°.9 the phenomenon does not appear, but returns at 97°.8. Moreover, the conversion at the latter temperature exhibits the plain character of a conversion above the transition temperature. From this series I already gained the impression that the maximum occurring at 76°.2 and 83°.0 has nothing to do with the conversion $S_{ch} \rightleftharpoons S_{mon}$.

One might imagine that, during the time corresponding with the falling branches in A and B fig. 2, so much S, has been regenerated that at the subsequent rises of the temperature one does not arrive any longer above the line AC in fig. 1. True, that difficulty