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The following papers were read:

**Chemistry.** — "*The melting point lines of the system sulphur + chlorine.*" By Prof. H. W. BAKHUIS ROOZEBOOM and A. H. W. ATEN.

(Communicated in the meeting of January 30, 1904).

The boiling point lines of this system have already been described at the meeting in May 1903. These led to the view that the compound  $S_2Cl_2$  in the liquid and vaporous condition is but very little dissociated and also that further compounds occur at a not too low temperature in liquids with a higher proportion of chlorine.

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A closer study of the changes in volume which take place in these liquids and of the velocity with which this happens has rendered it probable that  $\text{S}_2\text{Cl}_2$  is chiefly formed and in addition also  $\text{S}_2\text{Cl}_4$ .

The equilibrium between  $\text{S}_2\text{Cl}_2$ ,  $\text{S}_2\text{Cl}_4$ ,  $\text{S}_2\text{Cl}_6$  and  $\text{Cl}_2$ , which takes place in the liquids is not modified to any extent by cooling below  $0^\circ$  and remains totally unchanged at those low temperatures at which these mixtures may deposit solid substances. This gives rise, during the solidification, to very peculiar phenomena which, up to the present, have not been noticed with other systems but which may be explained by the views of the phase doctrine.

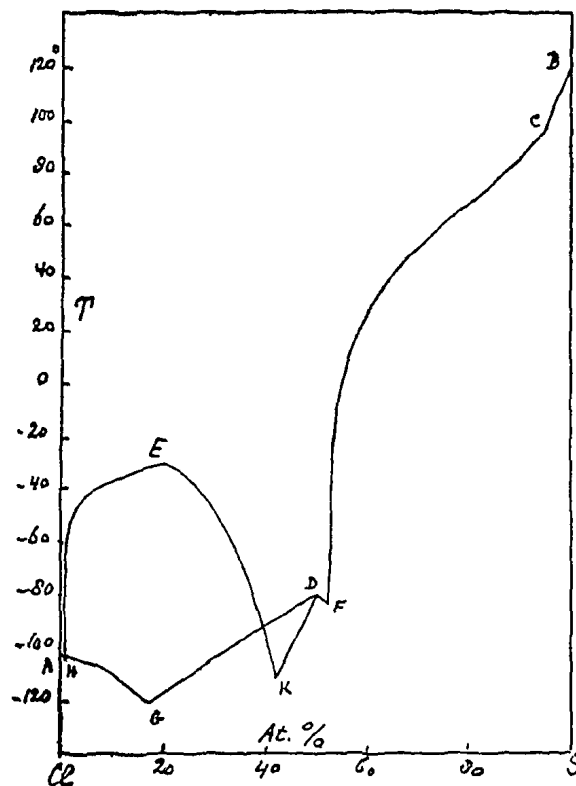


Fig. 1.

On the other hand nothing noteworthy occurs with mixtures containing 50—100 atomic per cent of S. These behave entirely like mixtures  $\text{S}_2\text{Cl}_2 + \text{S}$ . The melting point of  $\text{S}_2\text{Cl}_2$  ( $-80^\circ$ ) is lowered by sulphur to F; the melting point of sulphur is also lowered by  $\text{S}_2\text{Cl}_2$ , from B ( $120^\circ$ ) to F.

At a low temperature the solubility of S in  $\text{S}_2\text{Cl}_2$  is very small. The solubility or melting point line of S consists of two curved lines



This difference is further shown by the different crystallisation paths which on further cooling are traversed by mixtures of the same gross composition.

These crystallisation paths start in each of the regions mentioned from the point representing the melting point of the solid phase, that is from A, D and E respectively, and indicate the series of mother liquors which remain, during a continued cooling, at each temperature. The crystallisation paths in the first region end in HI or IG, those for the second in KI or IG, for the third in HI or KI. The lines I and II schematically indicate two similar paths in the last region, the vertical line EE' is a third one which applies to a liquid of the gross composition  $\text{SCl}_4$ .

As soon as the crystallisation paths arrive at HI, KI or GI, the subsequent solidification takes place along these lines, each time with deposition of two solid phases:  $\text{Cl}_2 + \text{SCl}_4$  on HI,  $\text{S}_2\text{Cl}_2 + \text{SCl}_4$  on KI and  $\text{Cl}_2 + \text{S}_2\text{Cl}_2$  on GI.

Finally the last liquid solidifies in I to a ternary eutecticum of the three phases.

This would be the state of affairs if — as has been said —  $\text{SCl}_4$ ,  $\text{S}_2\text{Cl}_2$  and  $\text{Cl}_2$  were miscible in all proportions without transformation.

If, however,  $\text{SCl}_4$  were a dissociable compound whose formation and decomposition led to complete equilibria at all solidification temperatures, then instead of the solidification described another would occur along the lines AH', H'E'K', K'D causing the system to appear as a binary one in which occurs a compound which enters into equilibrium with its components in the liquid condition. The position of these lines within the figure of the ternary system is determined by the degree of dissociation of the liquid compound. If this is extremely small, these lines approach to AH, HEK and KD, if very large they approximate to AG and GD and the compound does not appear as a solid phase. Solid  $\text{Cl}_2$  is deposited along AH', solid  $\text{SCl}_4$  along H'E'K', solid  $\text{S}_2\text{Cl}_2$  along K'D; H' and K' are two eutectic points where complete solidification takes place. These three lines are not only the first series of solidifying points of the different mixtures, but at the same time the crystallisation paths of all mixtures.

Now with mixtures of  $\text{S}_2\text{Cl}_2$  and  $\text{Cl}_2$ , neither the first nor the second case is quite realised. At the low temperatures at which the solidifications take place,  $\text{Cl}_2$ ,  $\text{S}_2\text{Cl}_2$  and  $\text{SCl}_4$  behave as independent components; for instance  $\text{Cl}_2$  and  $\text{S}_2\text{Cl}_2$  may be mixed in the liquid condition without entering into combination and in this way the two solidifying lines AG and GD (fig. 1 and 2) of these mixtures

have been determined. Neither does  $\text{SCl}_4$  undergo decomposition at those low temperatures. If, therefore, it were possible to isolate pure  $\text{SCl}_4$ , all imaginable mixtures thereof with  $\text{Cl}_2$  and  $\text{S}_2\text{Cl}_2$ , or with both might be obtained and the further portions of fig. 2 could then be constructed. This, however, is not the case.

On account of the extreme minuteness of its crystals and the low temperature at which crystallisation takes place, the compound  $\text{SCl}_4$  cannot be isolated in a pure condition and cannot, therefore, be added in definite proportions to  $\text{Cl}_2$  or  $\text{S}_2\text{Cl}_2$ . By exposing various mixtures of these compounds to temperatures of  $0^\circ$  and higher it is possible to cause the voluntary formation of those quantities of  $\text{SCl}_4$  which are in equilibrium with  $\text{Cl}_2$  and  $\text{S}_2\text{Cl}_2$  at the temperature chosen. As these do not change much with the temperature, the same series of mixtures is fairly well retained on cooling to the crystallisation temperatures. The number of ternary mixtures whose crystallisation may be investigated is, therefore, restricted to one for each gross composition.

We, therefore, always obtain for the first solidifying points a series such as  $\text{AH'E'K'D}$  in fig. 2, just as if we were dealing with a binary mixture in which a dissociable compound occurred. If, however, the equilibrium in the liquid does not change when  $\text{Cl}_2$ ,  $\text{SCl}_4$  or  $\text{S}_2\text{Cl}_2$  crystallises out, the system on solidification must behave as a ternary one.

This should have appeared in practice by the fact that the curve of the first solidifying points did not also represent the path of crystallisation, and, therefore, the mother liquor left after cooling each mixture to a lower temperature differed in composition from that given by the point on the curve corresponding with the temperature in question. Owing to the nature of the crystals, however, it was impossible to remove the mother-liquor with a pipette.

It was, however, possible to prove in the case of a liquid of the gross composition  $\text{SCl}_4$  that this does not completely solidify to  $\text{SCl}_4$  at  $\text{E}'$ , but only commences to deposit  $\text{SCl}_4$  at that temperature ( $-30^\circ$ ), which quantity increases on further cooling, but in such a manner that no complete solidification takes place below  $-80^\circ$ . In the points on both sides of  $\text{E}'$  the continuity is still more pronounced and this makes the accurate determination of even the first solidifying points very difficult.

In the second place the solidification of the different mixtures ought not to be complete in  $\text{H}'$  or in  $\text{K}'$ , but only in  $\text{I}$  after traversing the crystallisation paths  $\text{H'I}$  and  $\text{K'I}$ .

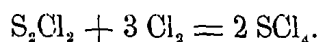
This is confirmed qualitatively but the exact determination of the lines H'I and K'I and consequently also of the ternary eutecticum proved to be impossible.

In this way no more was obtained than is indicated in Fig. 1, namely the solidification lines AG and GD for the mixtures of Cl<sub>2</sub> and S<sub>2</sub>Cl<sub>2</sub>, in which no compound had formed and besides these the series of the first solidifying points AH, HEK and KD for the partially combined liquids formed at 0°.

These lines therefore correspond with the accentuated lines in Fig. 2. The true melting point of SCl<sub>4</sub>, without decomposition of the liquid (E Fig. 2) is therefore not yet known. If SCl<sub>4</sub> could have been prepared in pure crystals, this might have probably been determined as it would presumably be situated below the temperature where the liquid compound shows perceptible decomposition.

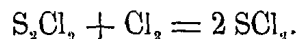
This is rendered more probable by the observation that notwithstanding their minuteness the crystals of SCl<sub>4</sub> when rapidly heated, are quite permanent up to -20°.

Fig. 1 does not agree with fig. 2 in an important point. In the latter DK is placed above DG, in the first DK is found below DG. DG represents the lowering of the melting point of S<sub>2</sub>Cl<sub>2</sub> by added Cl<sub>2</sub>, when this remains unchanged: DK when a portion of it combines with a part of the S<sub>2</sub>Cl<sub>2</sub> to SCl<sub>4</sub>, according to the equation



If we now compare the total amount of the foreign molecules which occur along with the S<sub>2</sub>Cl<sub>2</sub>, for the same total amount of Cl<sub>2</sub>, these numbers are smaller in the case of a partial formation of SCl<sub>4</sub> than when this is not the case. According to this supposition DK ought to be situated higher than DG.

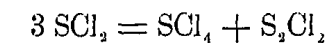
As in practice, the reverse position was found we must look for a cause which may explain this fact. We find this by supposing that besides SCl<sub>4</sub> there is also formed in the liquid a considerable proportion of SCl<sub>2</sub>, according to the equation



By taking this view the number of foreign molecules mixed with the S<sub>2</sub>Cl<sub>2</sub> becomes greater owing to the formation of SCl<sub>2</sub> than without this.

The formation in the liquid of an amount of SCl<sub>2</sub> exceeding that of SCl<sub>4</sub> which had already become probable by the dilatometric experiments has, therefore, been confirmed. The slow crystallisation of SCl<sub>4</sub> will now be better understood; but the liquids between Cl<sub>2</sub> and S<sub>2</sub>Cl<sub>2</sub> should now be considered not as ternary but as quater-

nary mixtures. If during the crystallisation  $\text{SCl}_2$  in the solution does not yield  $\text{SCl}_4$  according to the equation



solid  $\text{SCl}_2$  ought to be found somewhere on the way to complete solidification. This point could not be decided.

**Chemistry.** — “*Enzymactions considered as equilibria in a homogeneous system.*” By A. W. VISSER. (Communicated by Prof. C. A. LOBRY DE BRUYN).

(Communicated in the meeting of January 30, 1904.)

1. A number of facts exist which indicate that the reactions created by enzymes are reversible. CROFT-HILL<sup>1)</sup> succeeded in partly converting a concentrated solution of glucose into a disaccharide with the aid of maltase and reversibly the disaccharide into glucose. He supposed it to be maltose but afterwards EMMERLING<sup>2)</sup> proved it to be isomaltose; the fact however remains that maltase may cause a reversible formation of polysaccharides. Recently, CROFT-HILL<sup>3)</sup> has further proved that there is formed from glucose by means of maltase a new crystallised biglucose called revertose, he thinks it probable that also maltose may be formed<sup>4)</sup>. KASTLE and LOEWENHART<sup>5)</sup> and afterwards HANRIOT<sup>6)</sup> found that the fat-splitting enzyme lipase is capable of resolving butyricester into butyric acid and alcohol and on the other hand of forming the ester from the decomposition products. EMMERLING<sup>7)</sup> noticed the regeneration of amygdalin from nitrilglucoside-amygdalate and glucose under the influence of maltase. E. FISCHER and FRANKLAND ARMSTRONG<sup>8)</sup> prepared with the aid of Kefir-lactase a disaccharide from a mixture of galactose and glucose called isolactose, which up to the present could not be isolated in a state of purity. The same authors also found that kefir-lactase forms a disaccharide from glucose alone and that emulsin does the same from a mixture of glucose and galactose.

<sup>1)</sup> J. C. S. 73, 634 (1898).

<sup>2)</sup> Ber. 34, 600, 2206 (1901).

<sup>3)</sup> J. C. S. 83, 578 (1903).

<sup>4)</sup> All these experiments show that the substance supposed to be maltase still contains other ferments.

<sup>5)</sup> Am. Ch. J, 26, 533 (1901).

<sup>6)</sup> C. R. 132, 212 (1901).

<sup>7)</sup> Ber. 34, 3810 (1901).

<sup>8)</sup> Ber. 35, 3151 (1902).