

Citation:

A.H.W. Aten, On a new modification of sulphur, in:
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Greenwich may still need a correction, we have reckoned the longitude and also the latitude on the map from Jidda, Mecca-gate.

At the conclusion of this paper, which has proved that much advice and help has come to me from many sides, the only thing left for me to do, is to express my sincere gratefulness to all those from whom I have received this help.

Postscript.

(November 1912).

In order to investigate the accuracy of our time-determinations we had compared the results from the eastern and the western star, but in doing this no attention had been paid to the fact, that in most cases the times of observation of the two stars lie too far apart to neglect the rate of the chronometer in the interval.

Therefore this comparison has been made anew after correcting the differences E—W; the results, however, have not been materially changed. We now obtained

$$\begin{array}{ll} \text{Jidda 23 nights} & \text{E—W} = + 0^{\circ}.12 \\ \text{Mecca 13} & \text{,} \quad \quad \quad + 0^{\circ}.23 \\ \text{Together} & \text{E—W} = + 0^{\circ}.16 \pm 0^{\circ}.10 \end{array}$$

against before $+ 0^{\circ}.11 \pm 0^{\circ}.10$. The constant error in the zenith-distances would be found now $\Delta z = + 1''.2$ against before $+ 0''.8$, but just as before it is small.

As mean error of the difference from one night we now found $\pm 0^{\circ}.58$ and therefore as mean error of a time-determination from two stars $\pm 0^{\circ}.29$ against before $\pm 0^{\circ}.32$. The accordance of the two stars was somewhat improved.

Chemistry. — “*On a new modification of sulphur*”. By Dr. A. H. W. ATEN. (Communicated by Prof. HOLLEMAN).

Communicated in the Meeting of September 28, 1912.

This investigation originated in an observation by ARONSTEIN and MEIJHUIZEN¹⁾, who noticed that when a solution of sulphur in sulphur chloride (S_2Cl_2), supersaturated at the temperature of the room, is heated to 170° , no sulphur crystallises on cooling. I have afterwards repeated this experiment and demonstrated that the solution of S in S_2Cl_2 , which has been heated to 170° not only fails to deposit sulphur at the temperature of the room, but is even capable of dissolving a

¹⁾ Verhandelingen Kon. Akad. Wet. Amsterdam, 1898. 1.

considerable quantity of sulphur, about as much as the solution saturated at 20° originally contained¹⁾. It also appeared that the conversion, which has taken place here retrogrades very slowly, for after 20 days the quantity of dissolved sulphur had decreased but very little.

The sulphur which was added originally as rhombic sulphur and consequently was present in the liquid as S_8 apparently undergoes some conversion or other on heating, for after the heating some S_8 has disappeared. The question now arises: what has become of this S_8 ? Does it pass into another modification of sulphur or is there a compound formed of S with S_2Cl_2 ? At one time I thought I ought to arrive at the latter conclusion, because in other solvents metaxylene for instance, the same phenomenon could not be observed. KRUYT²⁾ on the other hand is of opinion that the cause of the disappearance of S_8 is situated in a transformation into amorphous sulphur S_{∞} . From what follows it will appear that neither of these views is correct.

I have again resumed the investigation of the above phenomenon in consequence of a publication by ROTINJANZ³⁾, in which are communicated the results of the determinations of the viscosity of sulphur at different temperatures with and without addition of iodine.

With molten sulphur without iodine, the course of the viscosity, as function of the temperature to which the sulphur has been heated, may be readily explained, because a transformation $S_8 \rightleftharpoons S_{\infty}$ takes place which proceeds comparatively slowly, so that with more rapid changes in temperature there exists no equilibrium between the two kinds of molecules. On rapid cooling, for instance the condition is such as corresponds with an equilibrium at a higher temperature. If, however, we endeavour to apply the same explanation to molten sulphur to which a trace of iodine has been added, we meet with difficulties as will be shown in a more elaborate article to appear shortly. The course of the viscosity cannot be explained here by the assumption that in the molten sulphur the above transformation $S_8 \rightleftharpoons S_{\infty}$ takes place. Presumably, a third modification of sulphur occurs here, as an iodine-sulphur compound does not exist, at least not in the solid condition. The same may now happen with mixtures of sulphur and sulphur chloride.

The investigation was, therefore, directed in the first place to decide what becomes of the S_8 when this is heated with S_2Cl_2 to a

¹⁾ Z. für physikalische Chemie. 54. (1905). 88.

²⁾ Z. für physikalische Chemie. 64. (1908). 545.

³⁾ Z. für physikalische Chemie. 62. (1908). 609.

suitable temperature. As has already been observed it is possible that either a compound of S with S_2Cl_2 is formed or else another sulphur modification. That, in this latter case, there can be no question of the formation of S_μ is shown readily from the following experiments.

On heating S with S_2Cl_2 , we can obtain very concentrated sulphur solutions. If this were caused by the formation of S_μ , this ought to have a great solubility, or the separation of S_μ ought to take place very slowly when, by heating, a concentrated solution of S_μ has been obtained. Neither of these phenomena occur, however. If sulphur which, owing to heating and rapid cooling, contains a certain quantity of S_μ is brought into contact with S_2Cl_2 , a turbid liquid is formed immediately. This turbidity of S_μ is permanent at the ordinary temperature, but on warming for a few minutes at 100° — 110° it disappears. On cooling, however, the turbidity at once reappears. Hence, it is shown that the solution and subsequent separation of S_μ is a process which takes place without appreciable retardation. At the temperature of the room, the solubility of S_μ is very trifling, for the experiment just described may be carried out with a very little S_μ . At a higher temperature the solubility is apparently fairly large. At 100° — 110° an appreciable, rapid transformation of S_μ takes place, presumably into S_2 , for if the above experiment is repeated a few times, the turbidity of S_μ , finally, does not reappear.

Not only in pure S_2Cl_2 , but also in S_2Cl_2 containing S_2 the solubility of S_μ is but small, although the solubility of S_μ in S_2Cl_2 is increased by addition of S_2 . For, on adding to S_2Cl_2 , which is turbid by S_μ a large quantity of S_2 , the turbidity disappears, but only when very little S_μ has been added. The possibility of the formation of S_μ in considerable quantities in solution is therefore excluded.

In order to ascertain what is formed from the S_2 originally present, the proper way would be to determine the melting point line of the system $S + S_2Cl_2$ after heating. It appeared, however, that nothing else but rhombic sulphur or S_2Cl_2 was separated. The newly formed product does not separate at all. As, moreover, no suitable chemical method could be found to separate the new product from the other, systematic determinations were carried out of the solubility of sulphur in mixtures that had been heated to a suitable temperature. From this it can also be shown whether a new modification or a compound has formed.

The system $S + S_2Cl_2$ must be treated as a ternary system, as besides S_2 and S_2Cl_2 , a third kind of molecule is present. The composition of a mixture that has been heated for a certain time must,

therefore be represented in a triangle the apexes of which indicate: S_2 , S_2Cl_2 , and the compound, or the new modification.

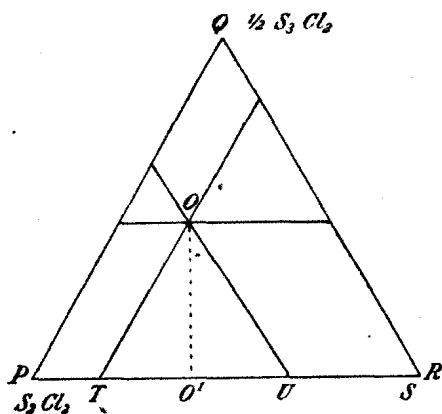


Fig. 1.

If O is the real composition, a mixture of this composition O contains $PTSRUS_2Cl_2$ and $UT\frac{1}{2}S_2Cl_2$. The gross composition is now:

$$\frac{\text{total } S}{\text{total } S_2Cl_2} = \frac{PT + \frac{1}{2}UT}{RU + \frac{1}{2}UT} = \frac{PO'}{RO'}$$

Hence, O' gives the gross composition. This is also the composition which one may determine experimentally by an estimation of the total sulphur. Not, however, the true composition O , for there is no means of determining the quantity of S_2Cl_2 .

The question now arises: If we heat the mixture of varying sulphur content to a given temperature and then cool to a definite temperature, how then does the composition of the solution saturated after warming, vary with the original composition? This is readily indicated with the aid of fig. 2.

Let the line $PBHR$ represent the equilibrium $S + S_2Cl_2 \rightleftharpoons S_2Cl_2$ at a temperature T_1 .

Let $TDFU$ represent the solubility line of S_2 in mixtures of S_2Cl_2 and S_2Cl_2 at the temperature t_1 . The point T then represents the solubility of S_2 in S_2Cl_2 .

When now a mixture of S and S_2Cl_2 of the gross composition A is heated long enough at T_1 the equilibrium $S + S_2Cl_2 \rightleftharpoons S_2Cl_2$, which belongs to the temperature T_1 , sets in. The inner composition is, therefore, given by a point of the curve $PBHR$, which is found by drawing a line $\perp PR$ in the gross composition of A . The intersecting point of this perpendicular line with $PBHR$ gives the looked for real composition. If one now cools rapidly to t_1 the composition B

will not alter if the equilibrium at T_1 remains the same. This liquid now must separate sulphur at t_1 ; the saturated solution must lie on

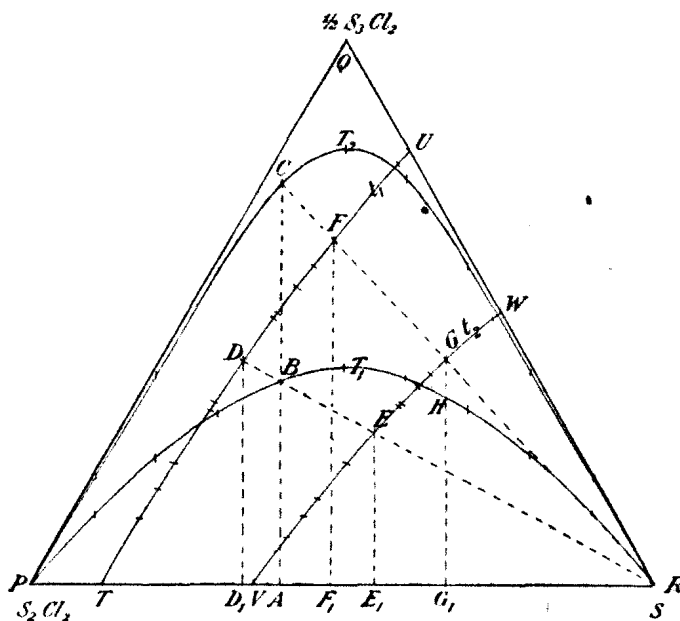


Fig. 2a.

the line $TDFU$. Its composition is found by drawing from R a straight line through B until this intersects the solubility line $TDFU$. In this manner we find for the real composition of the saturated solution D , the corresponding gross composition is D_1 .

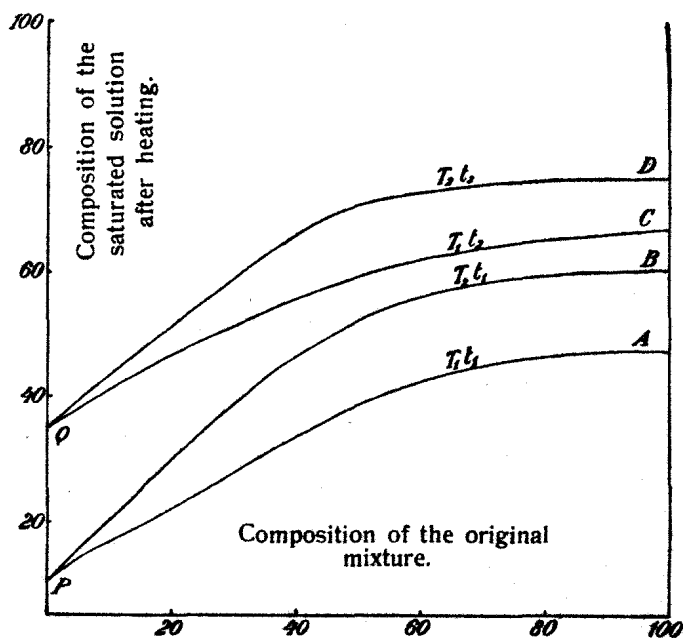


Fig. 2b

We can carry out this construction for different gross compositions and then put down the composition of the solutions saturated at t_1 after heating at T_1 as function of the original composition. We then find the line PA in Fig. 2b.

When we determine the solubility line at a higher temperature t_2 , the line QC is found. If we heat at a higher temperature T_2 and again determine the solubility at t_1 and t_2 , the lines PB and QD are found.

We see that these lines, at 100 at. % S of the original composition, approach to a certain limitation value which is different for different temperatures of heating and of solubility. This limitation value can give a larger as well as a smaller sulphur content than corresponds with the composition of the compound.

The first is the case when the compound is but little dissociated and the solubility of the sulphur is great, the latter when the dissociation is great and the solubility small.

Quite different becomes the course of these solubility lines when a new modification of sulphur is formed. In this case, the composition of a ternary system is given by a point in a triangle the apices of which indicate S_2 , Cl_2 , S_A and the new sulphur modification. We then obtain the gross composition (for instance D_1 in Fig. 3a)

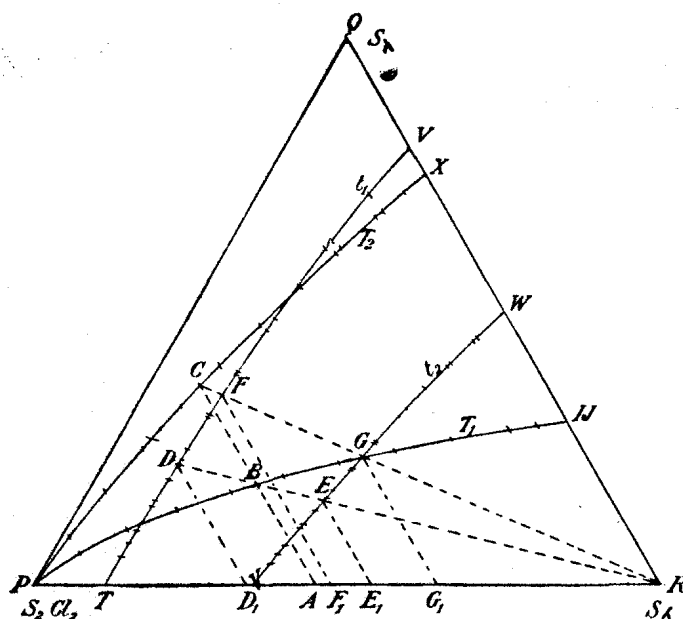


Fig. 3a.

by drawing a line $// QR$ through D which indicates the real composition. The line indicating the inner equilibrium between S_A and

the new modification of sulphur will now have the course of $PBGY$ in Fig. 3^a for a temperature T_1 . The solubility line of S_2 in mixtures of S_2 and Cl_2 and the new modification will be $TDFV$ at the temperature t_1 .

We can now deduce in exactly the same manner as in Fig. 2^a

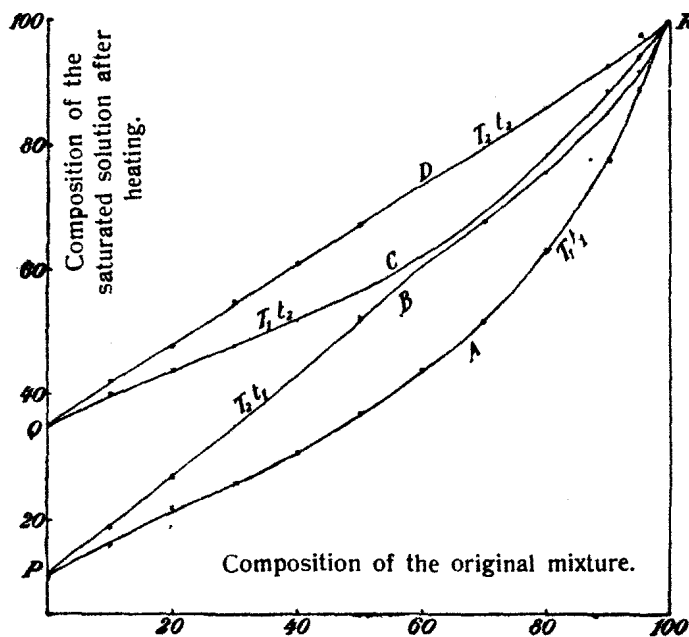


Fig. 5b.

what is the gross composition of a given mixture, which after heating to T_1 is saturated with S_2 at t_1 . If we do this with different compositions we find that the composition of the saturated solution as a function of the original composition is given by the line PAR in Fig. 3^b. If we repeat the same construction for mixtures which are heated to T_2 and for solubilities at t_1 and t_2 we find the lines PBR , QCR and QDR . These lines all converge in one point. At 100 at. % S of the original composition, the composition of the saturated solution is also 100 at. % S the temperature to which the mixture was heated or independently of temperature at which the solubility has been determined.

Hence, there exists a characteristic difference between the course of the solubility line with a compound and a new modification. Therefore, it was expected that in this manner we might decide with which of the two cases we are dealing here.

Before proceeding to the actual solubility determinations it was ascertained at what temperature the transformation of S_2 becomes

perceptible and how long the heating must be continued before the equilibrium is attained. It now appeared that a very perceptible conversion already occurs at 100°. Whereas, at 0° the solubility of S_2 in S_2Cl_2 , without previous heating amounts to 36.1 at. % of S, this, after heating to 100°, becomes 55.7 at. % of S for a 50 at. % mixture. The heating, therefore, causes a considerable increase in solubility. It also appeared that at 100° 1½ hour was required for the equilibrium to set in. This reaction, therefore, proceeds at 100° comparatively slowly and it may be expected that by rapid cooling the equilibrium can be fixed at 100°. Above 100° it is different. Because, as a rule, the velocity of a reaction for every 10° of rise in temperature becomes 2—3 times greater, the setting in of the equilibrium will, at 140°, require about 5 minutes and at 170° less than one minute. Here we shall not be able to cool so rapidly that the equilibrium becomes fixed and hence we shall find, after heating to 170°, somewhat fluctuating values for the solubility. This explains why the determinations previously carried out at 170° agreed badly. At a lower

TABLE I.

Original composition at % S	Composition of the saturated solution at		
	25° at % S	0° at % S	— 60° at % S
0	53.5	36.1	11.6
10.0	57.6	40.1	18.1
28.7	62.0	47.4	31.9
49.6	—	55.7	—
49.9	66.6	56.0	42.9
60.1	69.4	59.9	47.7
69.1	72.8	—	—
79.4	—	72.0	65.2
80.1	—	71.6	66.1
89.9	82.1	—	—
90.1	—	80.5	—
94.6	87.7	—	—
97.4	91.0	—	—
98.0	93.5	—	—

temperature than 100° , the completion of the equilibrium takes a longer time and it can be fixed with still greater certainty.

The method of investigation is very simple. A mixture of sulphur and sulphur chloride is heated for a sufficient time at the desired temperature. The liquid is then cooled rapidly, sulphur is added if the solution is not already saturated and the whole shaken at the temperature at which we want to know the solubility. When the solution is saturated a sample of the liquid is taken and its composition determined. This determination is carried out by oxidation with *aqua regia* and bromine, evaporation of the volatile acids and titration of the residual sulphuric acid.

In the first place, mixtures of varying composition were heated to 100° and the solubility determined at 25° , 0° and -60° .

The results are united in table I. (see p. 579).

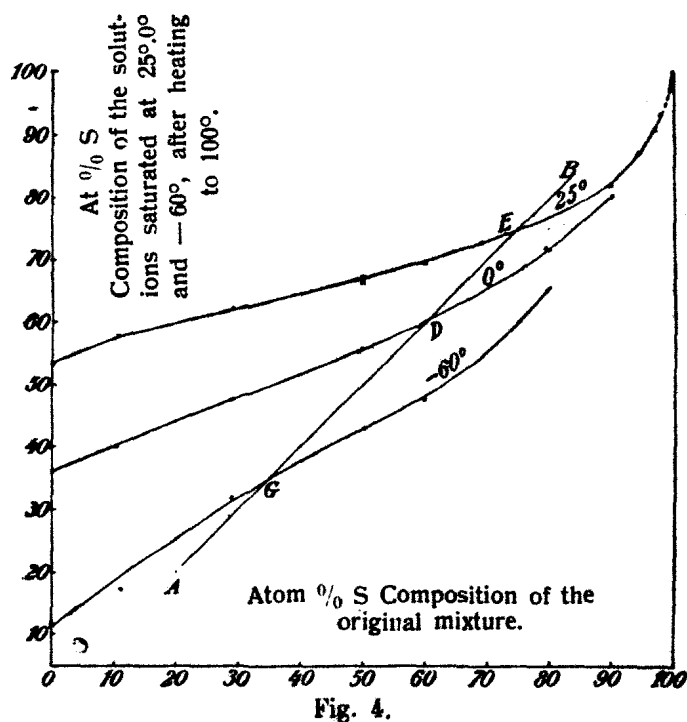


Fig. 4.

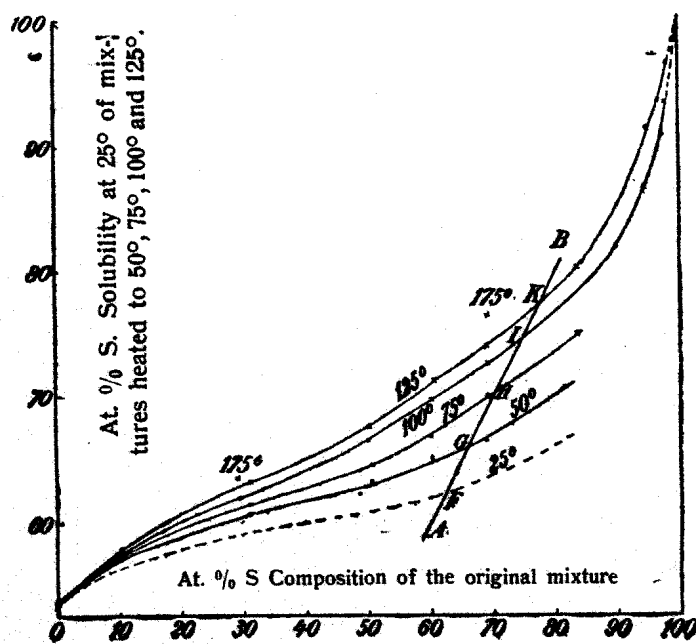
If we represent graphically the relation between solubility and original composition we obtain the lines shown in Fig. 4.

A comparison of these lines with those of Figs. 2^b and 3^b shows that they correspond with the lines of Fig. 3^b which are drawn in case a new modification is present. The solubility line for 25° , in particular, proceeds very distinctly towards 100 at % of S.

In the second place, mixtures of varying composition were heated

TABLE II.

Original composition in at. % S	Composition of the solutions saturated at 25° in at. % S, after heating to			
	50°	75°	100°	125°
0	53.5	53.5	53.5	53.5
10.0	57.2	57.9	57.6	57.9
28.7	—	—	62.0	—
30.9	60.7	61.5	—	63.2
50.3	63.2	64.4	—	67.6
60.1	65.0	66.7	—	71.3
69.1	66.6	70.9	72.8	74.1
81.4	70.6	—	—	—
83.7	—	75.0	—	80.1
89.9	—	—	82.1	—
94.6	—	—	87.7	—
94.9	—	—	—	91.5
96.8	—	—	—	93.6
97.4	—	—	91.0	—
98.0	—	—	93.5	—
98.1	—	—	—	95.6



to 125°, 100°, 75° and 50° and the solubility determined at 25°. The values found are given in table II.

From the line of 125° we see, still more distinctly than from that at 100°, that this proceeds towards 100 at. % S in accordance with the line deduced in case a new modification is formed.

No experiments could be carried out with quantities of sulphur larger than indicated in the table. Not at 50° and 75° because the liquid at these temperatures was not homogeneous. Not at 100° and 125° because the liquids rich in sulphur are very viscous and, therefore, cannot be separated from the crystals by centrifugal action.

The line drawn for 25° has not been determined experimentally, but has been found by extrapolation of the values at 50°, 75°, 100° and 125°. We notice from this line that even at 25° a considerable amount of the new sulphur form must be present. A comparison of the lines for 25°, 50°, 75°, 100° and 125° shows that the quantity of the new modification increases at a higher temperature and that this increase for each 25° difference, is greatest below 100°; from 100° to 125 the solubility increases but little. For this reason, when the liquids are heated at 175°, we find but a small increase in solubility, as shown by the two points drawn in Fig. 5. We must, however, bear in mind that at 175°, the equilibrium will not be fixed. If such were the case a somewhat greater solubility would have been found.

The existence of a new modification of sulphur, has not, however, been proved with absolute certainty by the course of the lines in Fig. 5. It might yet be possible that a compound was formed very rich in sulphur, such as S_{16} , S_2Cl_2 , which contains 94 at. % of sulphur. In such case the existence of these liquids rich in sulphur would be explained. The line in Fig. 5 then ought not to proceed in the extrapolated part towards 100 at. % of S, but turn to the right and attain say at 96 or 98 at. % of S their limitation value.

That, however, a new modification is actually formed is shown in the following manner.

When in mixtures of sulphur and sulphur chloride a new modification is formed on heating, this must also be the case with pure sulphur although perhaps in smaller quantities than in mixtures with S_2Cl_2 . Moreover it may be — and there is reason to suppose so — that the conversion of the new modification into S_8 , or reversely, proceeds more rapidly when no or little S_2Cl_2 is present. This might be the reason why the formation of that new modification in pure sulphur could not be demonstrated.

We have succeeded however, in demonstrating that the new modification is formed in pure sulphur also. When sulphur is heated to 125° , rapidly poured out and powdered and then placed into S_2Cl_2 , the solubility is larger than that of rhombic sulphur alone.

In this way was found :

1. Sulphur after heating to 125° and rapid cooling mixed with S_2Cl_2 , to 69.2 at. % of S. Solubility = 56.0 at. % of S.

2. Id. Mixed with S_2Cl_2 , to 73 at. % of S. Solubility = 56.5 at. % of S.

3. Id. Mixed with S_2Cl_2 , to 80.9 at. % of S. Solubility 58.5 at. % of S.

The solubility at 25° for sulphur, which has not been heated, is only 53.5 at. % of S. The heated sulphur has, therefore a considerably larger solubility than the non-heated rhombic sulphur, which proves that in the heated sulphur another modification is also present. It has already been explained above that this cannot be amorphous sulphur. But it is also shown by the fact that the sulphur content of the saturated solutions is all the greater when more sulphur is added. Now, the solutions 1—3 indicated above are all saturated with amorphous sulphur for this was present in large excess. If now the increase in solubility were caused by the amorphous sulphur getting dissolved, the solubility from 1—3 ought to be the same. To make more sure, the solubility of a mixture of rhombic and amorphous sulphur at 25° was determined also. For this was found 54.5 at. % of S. Even after 24 hours the solution was still somewhat turbid owing to amorphous S. The figure 54.5 at. % of S is therefore too high. Hence, it appears again that the solubility of amorphous sulphur is very slight and cannot explain the increase of solubility in experiments 1—3.

In connection with his theory of allotropy, Prof. SMITS has pointed out, that the system sulphur must be a ternary system. The possible relation between the sulphur modification we were dealing with, and that assumed by Prof. SMITS, will be discussed in a following paper, as well as the results of investigations on the molecular weight and the permanency of the modification, which are now being carried out.

Amsterdam, Chem. Lab. University.

August 1912.

Chemistry. — "*On the relation between the sulphur modifications.*"

By Dr. H. L. DE LEEUW. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of September 28, 1912).

Prof. SMITS has authorised me to criticise a recently published report of a lecture by KRUYT delivered before the Deutsche Bunsen Gesellschaft (Z. f. Elektr. Chem. 1912, 10, 581) and to make use for this of the experimental data obtained during a research conducted by me as private assistant. Before proceeding to this it seems to me desirable to mention very briefly some points in historical order.

SMITH and his coadjutors were the first to assume dynamic isomery with sulphur. They determined the course of the equilibrium line S_α — S_μ and also the solidification line of the monoclinic sulphur. KRUYT, in addition, determined the initial melting points of rhombic sulphur which, at different temperatures, had got into equilibrium with S_μ , the melting point line of SMITH being used as the method of analysis. Moreover, he concluded to the existence of a metastable region of demiscibility contrary to SMITH and his co-workers who rejected this.

By Prof. SMITS it was pointed out already in 1910 that the results of the sulphur investigation contain data which support his theory of allotropy. KRUYT, for instance, had stated that when starting with rhombic sulphur, which has placed itself in equilibrium at 90° and then determining the melting point of the sulphur in this condition, according to SOCH's method, $110^\circ.9$ was found whereas, in the same method of working, a melting point of $111^\circ.4$ was observed when the S had come into equilibrium at 65° . From this result it, of course, follows that we are dealing here with an inner equilibrium in the solid state, therefore with mixed crystals, and that the line for the inner equilibrium in the solid condition proceeds on increasing the temperature, to a greater S_μ content, as in the liquid. Prof. SMITS therefore changed the T, x -figure (fig. 1) into that indicated in fig. 2.

Afterwards, A. SMITH and CARSON (Z. f. phys. Chem. 1911, 77, 661) have determined the solidification line of S_{Rh} also making use of the lines determined previously. This line differs a little with the curve of KRUYT. Moreover, they also found a third melting point line, that of the "soufre nacr  ". In the same time KRUYT (Chem. Weekblad 1911, 647) announced that all the values of the transition temperature ($T \rightarrow$), with varying quantities of S_μ are situated lower than REICHER's value ($95^\circ.6$) and also that the dimensions of the mixed crystal-region are not such that the influence thereof on his calculations exceeds the experimental errors.