Chemistry. — *"A Third Kind of Sulphur Molecule"*. (Fifth Communication). By Dr. A. H. W. ATĖN. (Communicated by Prof. A. F. HOLLEMAN.)

(Communicated in the meeting of Oct. 27, 1917).

1. *Introduction.*

In the first publication on this subject [1]) the solubility of rhombic sulphur was treated in mixtures of sulphur chloride and sulphur, which were heated to temperatures of 75°—175°, and were then quickly cooled down. It then appeared, that this heating greatly enhanced the solubility of rhombic sulphur. This phenomenon is explained in this way, that the rhombic sulphur, when heated with sulphur chloride, is converted to another form of sulphur, S_π .

The question how sulphur behaves, when it is heated with other solvents, has only been briefly treated in the preceding communications.

What had appeared was, that the conversion of S_λ into S_π takes place at 100° not only in sulphur chloride, but also in carbon sulphide. To enable us to make a better comparison between sulphur chloride and other liquids as solvent, the solubility of rhombic sulphur was determined in mixtures of sulphur and toluene, which had been heated to different temperatures.

2. *Increase of solubility of sulphur by heating in toluene-solution.*

The solubility of rhombic sulphur in toluene amounts to 0,92°/₀ at 0°. When a solution of sulphur in toluene is heated at 150° for some hours, it is found that after cooling the solubility has become greater at 0°, and the more so as the original solution contained more sulphur. This is accompanied by a change of the colour of the solution. A solution of S_λ in toluene is almost colourless at 0°. After being heated the same solution exhibits the yellow colour of S_π at 0°. From this follows that also in toluene S_λ is partly converted into

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[1]) Zeitschr. f. physik. Chem. **81**, 257 (1912). Following communications ibid **83**, 442 (1913); **86**, 1 (1913); **88**, 312 (1914).

S_π. From the increase in solubility of rhombic sulphur in toluene after heating, the quantity of S_π formed can be calculated.

In the first place it now appeared that the equilibrium $S_\lambda \rightleftarrows S_\pi$ sets in much more slowly in toluene than in sulphur chloride. In toluene it is about six hours at 140° before the equilibrium has been established, whereas in sulphur chloride at the same temperature only a few minutes are required for it. (First communication, p. 265). In view of this 140° was chosen as lowest temperature at which determinations were made. Determinations were also carried out at 150° and 160° to study the influence of the temperature on the equilibrium.

The determination of the solubility of sulphur in toluene after heating took place as follows: A mixture of toluene and sulphur of known concentration was heated for six hours at 140°, for four hours at 150° or for two hours at 160°, and then rapidly cooled, in which part of the sulphur separated. After addition of a small quantity of rhombic sulphur the mixture was stirred for an hour at 0°. Then a sample was taken from the solution, and the sulphur content was determined by evaporation of the toluene.

The results are given in Table I. In figure 1 the solubility of the sulphur after heating, is graphically represented as function of the concentration of the mixture.

TABLE I.

140°		150°		160°	
Concentra-tion of the solution	Solubility at 0°	Concentra-tion of the solution	Solubility at 0°	Concentra-tion of the solution	Solubility at 0°
3.4 %	1.18 %	3.6 %	1.24 %	3.2 %	1.24 %
6.2	1.42	6.6	1.50	6.2	1.54
9.2	1.64	10.6	1.79	15.0	2.40
22.0	2.69	22.6	2.96	21.6	3.00
27.6	3.23	30.1	3.54	30.0	3.64

The lines for 140°, 150°, and 160° stop at about 36, 41, 47°/₀ sulphur, mixtures of a higher sulphur content not being homogeneous at these temperatures. [1])

[1]) KRUYT. Zeitschr. f. physik. Chemie 65, 502, (1909).

Fig. 1

Composition of the mixture in % *S*.

(y-axis) Solubility at 0° in % *S*.
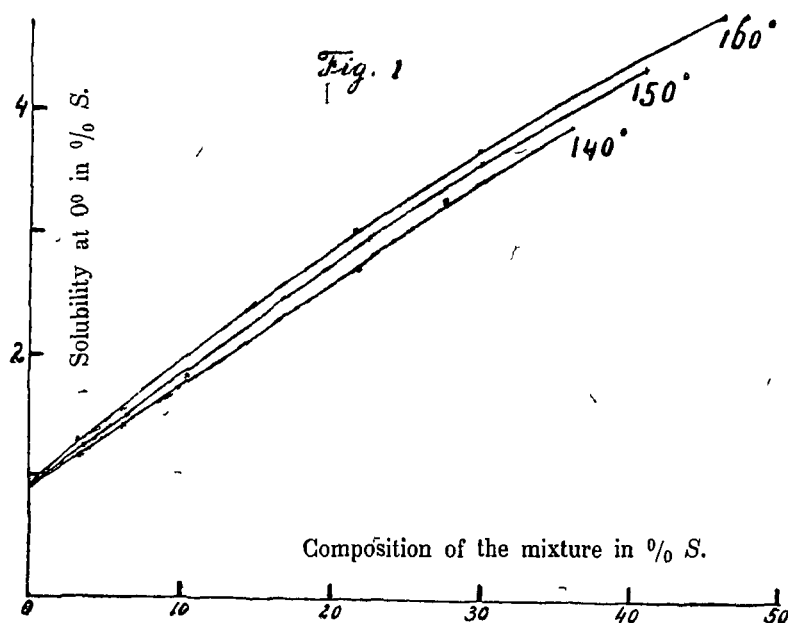
3. *The equilibrium* $S_\lambda \rightleftarrows S_\pi$ *in solutions in toluene.*

From the solubility of rhombic sulphur in toluene, after the solution has been heated, the quantity of S_π that is present in the solution can be calculated. Thus we know the equilibrium $S_\pi \rightleftarrows S_\lambda$ in a solution of given concentration at a given temperature.

When we call the solubility of rhombic sulphur at 0° *S*, the S_π-content of the solution is given by:

$$S_\pi = 0.68 \; (S - 0.92)$$

(4$^{\text{th}}$ communication). In this way we find, in case of equilibrium, the quantities S_π and S_λ present, which are given in table II.

TABLE II.

140°		150°		160°	
S_λ	S_π	S_λ	S_π	S_λ	S_π
8.6	0.51	9.2	0.63	8.1	0.63
15.2	0.97	16.0	1.11	15.0	1.20
21.4	1.39	24.2	1.67	31.9	2.82
43.0	3.37	43.7	3.90	42.1	3.96
50.3	4.39	53.2	4.96	53.0	5.13

To facilitate a comparison with the values of sulphur chloride, these values are expressed in atom percentages.

These lines of equilibrium for 140° and for 160° are drawn in figure 2 on rectangular coordinate paper. It appears from these lines that the S_π-content at 160° is only little higher than at 140°. In this range of temperature an important shifting of the equilibrium does, therefore, not take place.
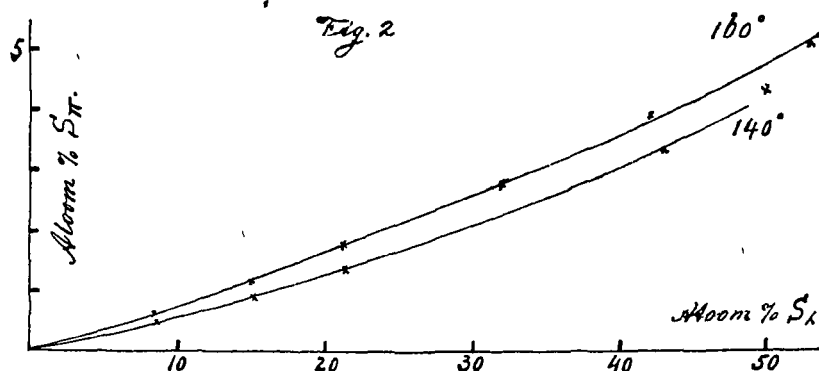
Seen from below the lines are convex, i.e. with increasing total sulphur content the relative quantity of S_π increases more than the relative quantity of S_λ. From this follows that the toluene present shifts the equilibrium towards the side of S_λ. In very dilute solution, where the quantity of toluene is practically constant, the equilibrium must move towards the side of S_π with increasing dilution, as the molecule S_π is smaller than the molecule S_λ (fourth communication p. 369). The accuracy of the experiments in case of great dilution is, however, not sufficient to allow us to demonstrate this.

4. *Comparison of the equilibrium $S_\lambda \rightleftarrows S_\pi$ in toluene and in sulphur chloride.*

In order to be able to compare the quantity of S_π in toluene with that in sulphur chloride, we must also calculate the quantities of S_π and S_λ, present in case of equilibrium, for these latter solutions from the solubility of rhombic sulphur. This is, however, not possible without further suppositions about the course of the solubility lines of S_λ in mixtures of S_π with sulphur chloride.

The course of these solubility lines being unknown, only a probable situation of the equilibrium $S_\lambda \rightleftarrows S_\pi$ in sulphur chloride can be given, and this in the following way:

We assume a certain situation for the line of equilibrium $S_\pi \rightleftarrows S_\lambda$, and construct the solubility lines for 25°, 0°, and — 60° with this line and the values of the solubility in Table I of the first communication.

From the more or less probable form of the solubility lines found thus, we can then decide whether the assumed line of equilibrium is more or less probable.

Thus it has been assumed in figure 3 that the line of the equilibrium $S_\lambda \rightleftarrows S_\pi$ in sulphur chloride at 100° has the same form as in toluene at 140°.

Fig 3
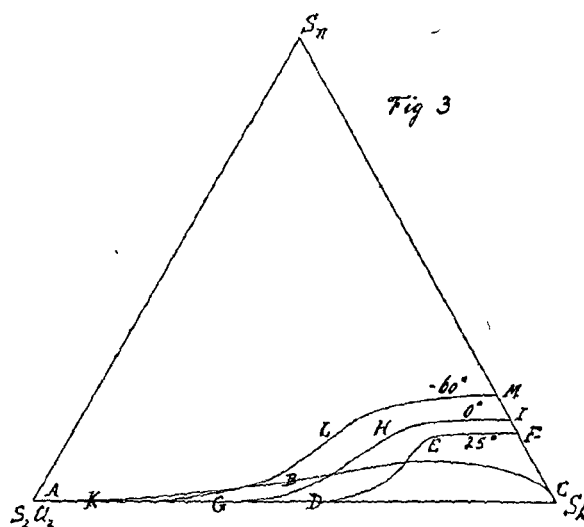
This line is $A B C$ in figure 3, the part $B C$ is extrapolated, except the point C. From this line we find for the solubility curves at 25° $D F F$, at 0° $G H I$, at —60° $K L M$.

The course of these solubility lines is very improbable. In the first place, according to these lines the solubility of S_λ in sulphur chloride would be greatly enhanced by S_π, especially at — 60°. For sulphide of carbon, in which S_λ dissolves almost equally well as in sulphur chloride, the solubility of S_λ is, on the contrary, but little increased by S_π (3rd communication 2, 3, 4). It can, therefore, not be accepted that by addition of S_π the solubility of S_λ is so much increased, as is drawn in figure 3.

· In the second place the points M, I and F, which indicate the solubility of S_λ in pure S_π at — 60°, 0°, and 25°, lie very close together, and at a very great S_λ-content.

This would mean that rhombic sulphur, even at — 60°, would possess a solubility in S_π of 77 %. This, too, is improbable, because

in the best solvents, sulphur chloride and sulphide of carbon, the solubility only amounts to $10\,\%$ at the same temperature.

The line of equilibrium $S_\lambda \rightleftarrows S_\pi$ in sulphur chloride must, therefore, be drawn so that the solubility lines run more steeply at D, G, and K, and that the points F, J, and M get to lie farther apart.

This is satisfied in figure 4.

The situation of the solubility lines drawn here, is however not probable either, for here the solubility of S, in sulphur chloride would be lessened by addition of not too large quantities of S_π.
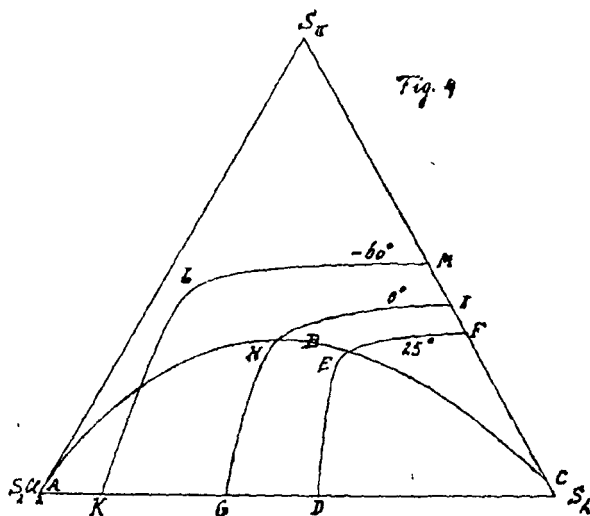
If, however, the homogeneous equilibrium line is given a form as $A B C$ in figure 5, we arrive at a plausible shape of the solubility lines. It is therefore probable that in figure 3 the line of the equilibrium $S_\lambda \rightleftarrows S_\pi$ lies too low, in figure 4 too high, and that figure 5 gives about the true situation. We may, therefore, assume the equilibrium $S_\pi \rightleftarrows S_\lambda$ in sulphur chloride at $100°$ in a mixture of 50 at. $\%$ of total sulphur to lie at about 25% S_π. In toluene the equilibrium mixture at $140°$ contains not quite 5 at. $\%$ S_π. Accordingly sulphur chloride has a particularly specifically favourable influence on the formation of S_π. That this is not exclusively caused by the greater solubility of S_λ in sulphur chloride, appears from an observation recorded in the third communication. It was found there that a solution in sulphide of carbon with 56 at $\%$ of

59

-7-

total sulphur contains only about 3 at. % of S_π at 100°, when the equilibrium $S_\pi \rightleftarrows S_\lambda$ has been established.

Fig. 5
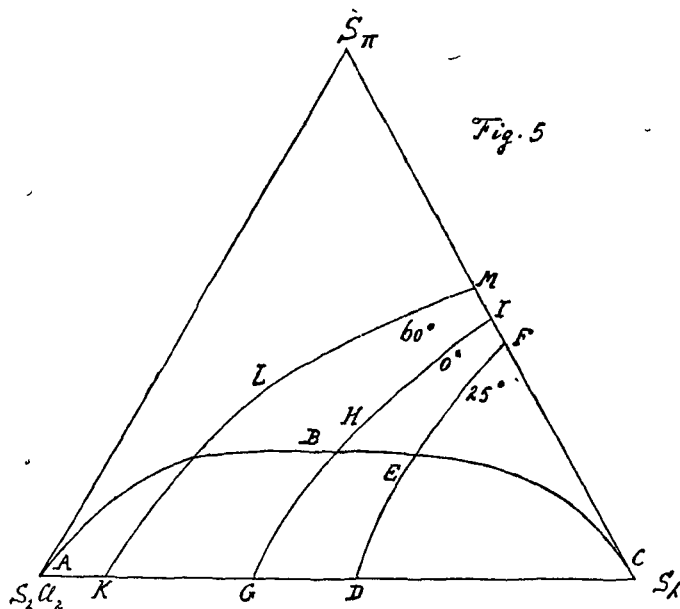
The quantity of S_π, which is formed in sulphide of carbon, is therefore much smaller than in sulphur chloride, and of the same order of magnitude as in toluene.

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