CVIII.—*Internal Equilibrium in Liquid Sulphur. Part I.*

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THE commonly accepted view as to the nature of liquid sulphur is that it contains, when in internal equilibrium, at least two molecular species, S_λ and S_μ. Attempts to estimate the relative proportions of the two forms present at different temperatures have been made by Alex. Smith and his collaborators (Smith and Holmes, *J. Amer. Chem. Soc.*, 1905, **27**, 979; Smith and Carson, *Z. physikal. Chem.*, 1907, **57**, 685), and their results are embodied in the familiar internal-equilibrium curve for liquid sulphur. The data from which their curve (see Fig. 1) was plotted were obtained by heating specimens of sulphur in open tubes until internal equilibrium had been reached at various temperatures between the melting and boiling points of sulphur, the liquid being then poured into ice-water to fix the equilibrium. Specimens chilled from below about 150° solidified rapidly into hard drops; on the other hand, when higher temperatures were used, the cooled mass was plastic and was kept for several days until it had hardened sufficiently to be ground. The dried and powdered specimens were then extracted, under standardised conditions, with carbon disulphide in a Soxhlet apparatus, and the amount of insoluble sulphur was estimated. If the amounts of insoluble sulphur thus found be taken as a measure of the amounts of S_μ present in the original specimens of liquid sulphur, an allelotropic line can be plotted.

It is, however, difficult to believe that this allelotropic line really represents the internal equilibrium in liquid sulphur. It is unlike any other such line at present known. Its course implies a large and rapid change in the magnitude of the heat of transformation of S_λ into S_μ between 170° and 200°, at which point the curve becomes practically vertical, the heat of transformation in consequence becoming negligible and the equilibrium composition independent of temperature. Smith and Holmes (*loc. cit.*) were aware of the difficulties in the way of the ordinary physical interpretation of the results, for they say that " caution is necessary in the interpretation of the data in regard to sulphur supercooled from very high temperatures," and that " such data should be used only for comparing the effects of variables other than temperature." In short, before we can accept the line, we must be satisfied that the sudden change of direction of the line to the vertical at about 160—170° is not due to the rate of chilling of the sulphur being insufficient to prevent reversion of S_μ to S_λ. The extent to which this reversion occurs will depend on the conditions of experiment, and in particular on (1) the size of the droplets as they fall into the ice-water, and (2) the speed with which they are transferred from the heating apparatus into the ice-water. If, therefore, the vertical part of the so-called allelotropic line is caused by ineffective chilling, a finer division of the liquid sulphur and a method of transference from the heating apparatus to the chilling vessel more rapid than pouring should at least transfer the vertical part of the line towards the S_μ axis.

In order to ensure as fine division of the liquid sulphur as possible we have made fine suspensions of liquid sulphur in a mixture of sulphuric acid and ammonium sulphate of approximately the same density as liquid sulphur. In order to accelerate transference from the heating vessel to the chilling bath, we have constructed an apparatus in which, by knocking a hole in the vessel containing the " emulsified " sulphur, the contents could be dropped straight into ice-water.

EXPERIMENTAL.

The Production of the Sulphur Suspensions.—The apparatus used consisted of a large boiling-tube that fitted into a cylindrical resistance furnace. The boiling-tube contained a mixture of 45 g. of recrystallised ammonium sulphate and 30 c.c. of concentrated sulphuric acid, and was fitted with a thermometer and a " bulb " stirrer at the end of a hollow glass tube mounted on a ball-bearing bicycle hub and driven by an electric motor. Experience showed that good suspensions of liquid sulphur in the molten acid sulphate could be obtained only with " bulb " stirrers, and that even with these the fineness of the suspensions varied considerably for a given speed of rotation.

It was found that the only effect of the acid sulphate on the sulphur was to oxidise it to an extent depending on the temperature. The production of sulphur dioxide was no disadvantage, because, although its anticatalytic effect on the rate of attainment of equilibrium made long heating necessary, its presence tended to prevent reversion on chilling. The sulphur as such was absolutely insoluble in the sulphate mixture. This point was tested by pouring the clear supernatant liquid from the melted sulphur into water, whereupon no sulphur separated.

To carry out an experiment, the semi-solid acid sulphate was heated with a flame until it was fused and its temperature raised a few degrees above that at which it was proposed to conduct a run. The electric heating furnace (which had been started some time previously) was now placed round the boiling-tube. The base of the furnace was closed with a removable asbestos cap, and as much of the top of the tube as possible was plugged with lead foil lined with asbestos to minimise heat loss and oxidation of sulphur. The stirring-motor was started and about 20 g. of powdered sulphur (recrystallised from carbon disulphide or toluene) were added in small quantities at a time over about 10 minutes. The thermometer in the mixture showed that if the furnace was allowed 3—4 hours in which to reach thermal equilibrium before the experiment started, the temperature did not vary by more than 1°. Stirring was rapid, though too fast running of the motor caused the liquid sulphur to stick to the stirrer and the walls of the tube.

Although internal equilibrium was reached in an hour even at the lower temperatures, it was found necessary to keep the sulphur stirred for 4—5 hours, especially at the higher temperatures when it was in the sticky state, before really fine suspensions could be obtained.

Chilling the Suspensions.—Passing through the hollow stirrer was a hard-glass rod which was kept clear of the liquid mixture by a coil-spring between a knob at the top of the rod and the bearing of the stirrer. In order to get the suspension out of the boiling tube, the cap at the base of the furnace was removed and, while the stirrer was still running, the top of the hard glass rod was struck with a mallet. The end of the rod knocked the bottom out of the tube and the contents fell directly into a large beaker of ice-water, which was kept rapidly stirred. The presence of ice in the water was a disadvantage, as the sulphur droplets tended to coagulate on it.

Analysis of the Chilled Sulphur.—Chillings from temperatures up to 150° readily gave fine droplets of sulphur that hardened rapidly. When obtained from higher temperatures, the droplets were sticky and required anything up to 5 days before they became hard enough to grind. The specimens were first washed in running water for 12 hours and then allowed to dry and harden on a porous plate in a vacuum desiccator. Fragments of broken glass from the boiling-tube were then picked out by hand. The yields, *before analysis*, were divided into two classes : those containing droplets of diameter up to 0·5 mm. were classified as " good," droplets up to 1 mm. in diameter were graded as " fair," and others rejected. When obtained from temperatures up to 160—170°, the size of the droplets made little difference to the content of S_μ; as will be seen, however, the amount of S_μ in samples from the higher temperatures differed considerably according to which grade they belonged to.

When hard, the specimens were ground in a mortar, sieved through a No. 30 mesh, and subjected to a further drying. The amount of insoluble S_μ was then estimated by Smith's method (see below). It was found necessary to extract and dry the extraction thimbles to constant weight before use, and to carry out all weighings as quickly as possible. About 8 g. of chilled sulphur were used in each extraction, which was carried out by allowing the thimble to fill and empty 6 times in 25 minutes. The residual insoluble S_μ was rapidly drained and allowed to dry in a vacuum desiccator to approximately constant weight.

As was found by Smith and Holmes (*Z. physikal. Chem.*, 1903, **42**, 474), so-called insoluble sulphur dissolves very slowly in carbon disulphide. To correct for this, those authors made a series of artificial mixtures of S_λ and S_μ and weighed the amounts of S_μ remaining after extraction; they thus obtained a curve which could be used to correct for loss of S_μ in any particular mixture extracted. Obviously the magnitude of the correction will depend on the particular extractor used, and is not of general application. We have attempted to estimate the effect of S_μ solubility in our experiments by continuing the extraction of specimens of chilled sulphur by a further 6 fillings of the Soxhlet thimble. Thus, in two experiments we found that 2·881 and 2·735 g. of extracted sulphur (*i.e.*,

S_μ) lost 0·086 and 0·091 g. on further extraction. This corresponds to a loss of under 3% on the S_μ present in 8 g. charges of unextracted sulphur. As this is within our experimental error, and having regard to the fact that we were more particularly concerned with temperatures at which the percentage of S_μ was considerable, we have not applied any correction to our results. The effect of a correction would be, of course, to raise the recorded percentages of S_μ found.

The data in Tables I and II refer respectively to those specimens of chilled sulphur droplets graded as " good " and " fair "; *T* gives the temperature at which the sulphur was allowed to attain internal equilibrium before chilling.

TABLE I.

T	150°	160°	170°	170°	175°	178°	180°	180°	186°	196°	210°
S_μ %	4·5	8·9	18·6	18·1	23·5	23·5	25·0	25·1	29·4	35·1	38·7
S_μ %	4·1	9·2	18·7	18·1	21·9	—	25·0	25·2	28·9	34·8	—
S_μ % (mean)	4·3	9·1	18·4		22·7	23·5	25·0	25·2	28·7	35·0	38·7
T	213°	223°	227°	229°	242°	260°	263°	271°	279°	280°	287°
S_μ %	38·8	37·1	39·0	40·8	39·6	38·6	37·7	39·9	37·9	39·3	39·5
S_μ %	—	37·0	—	40·5	39·6	38·5	—	—	37·9	39·2	40·4
S_μ % (mean)	38·8	37·1	39·0	40·7	39·6	38·6	37·7	39·9	37·9	39·3	39·9

TABLE II.

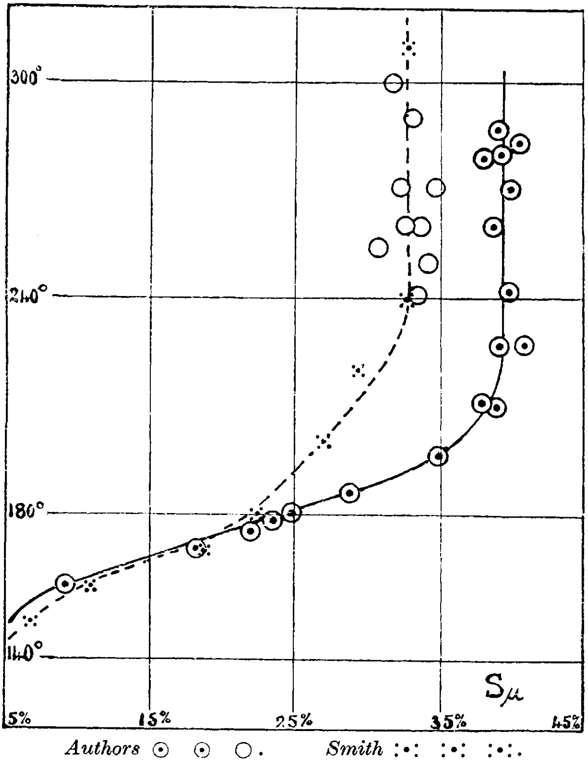
T	240°	245°	254°	260°	261°	266°	271°	271°	290°	299°
S_μ %	33·9	34·4	31·5	33·7	32·6	34·8	32·4	34·6	33·2	31·7
S_μ %	33·8	34·0	30·0	—	—	—	—	—	—	—
S_μ % (mean)	33·9	34·2	30·8	33·7	32·6	34·8	32·4	34·6	33·2	31·7

Conclusions.

The effect of our method of chilling liquefied sulphur has been, in the case of our most finely divided specimens (dotted circles ⊙ on diagram), to prolong the transverse portion of Smith and Holmes's allelotropic line and to arrive at an approximately vertical line at about 40% S_μ instead of at about 33%. As was pointed out above, this result is to be taken as implying that the cause of the vertical trend of the curve is to be found in ineffective chilling, a conclusion which is strongly supported by the fact that our less effectively chilled samples gave percentages of insoluble sulphur (plain circles on diagram) that lie on and about Smith and Holmes's curve. It is thus clearly incorrect to regard plots of the kind shown in the diagram as true allelotropic lines giving the relative amounts of S_λ and S_μ in liquid sulphur at different temperatures.

In connexion with the methods used by ourselves and by Smith and his collaborators for estimating the amounts of insoluble sulphur in chilled sulphur, it should be pointed out that we have no information as to what is happening to the chilled specimens while they are hardening. As Smith himself noticed (*loc. cit.*), sulphur in the plastic condition passes through the Soxhlet thimbles; how and why it does so is a matter for further investigation. The fact that quite definite changes in the properties of the sulphur occur during the process of hardening makes it questionable whether the amount of insoluble " hard " sulphur at the end of that period is in reality the amount of insoluble S_μ in the freshly chilled plastic mass. This point will be discussed in a subsequent communication.

FIG. 1.



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