XLI.—*Internal Equilibrium in Sulphur. Part II. Amorphous Sulphur* (S_μ) *as a Gel, and the Tyndall Effect in Liquid Sulphur.*

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It has long been recognised (Kruyt, *Z. physikal. Chem.*, 1909, **65**, 486; Hammick and Holt, J., 1926, 1995) that as molten sulphur is heated, it becomes richer in one or more forms which are less miscible with other liquids and give rise to the peculiar properties of liquid sulphur. It also appears to have been generally assumed, with Smith and his co-workers, that the insoluble, amorphous solid obtained when molten sulphur is chilled, allowed to harden, and then extracted with carbon disulphide, is identical with one of the constituents present in the melt. As is well known, the familiar allelotropic line (Smith and Carson, *Z. physikal. Chem.*, 1907, **57**, 685) giving the percentages of S_μ present in liquid sulphur at various temperatures is constructed from data derived from estimates of the amount of insoluble sulphur present in specimens of sulphur chilled from these temperatures.

In the course of our experiments on equilibria in the system sulphur–sulphur chloride (J., 1928, 1785), we noticed that in the presence of even quite small proportions of its chloride the element could be heated to 160—180° without any great increase in viscosity. For instance, mixtures of pure sulphur (98%) with sulphur chloride (2%) heated in sealed tubes for various periods (½—2 hours) at 140° and 180° gave quite mobile, dark-coloured liquids. Most of these mixtures on sudden chilling solidified almost completely, and it was found that a considerable proportion of the solid separating was insoluble in carbon disulphide, *i.e.*, the solid contained S_μ. In many of the tubes, however, solidification did not occur on chilling, and in some cases it was possible to open them and treat the contents with carbon disulphide while the latter were still metastable and fluid. The supercooled mixture was completely miscible with this solvent. It would thus appear that S_μ, insoluble in carbon disulphide, does not exist in the fluid sulphur–sulphur chloride mixtures that have been chilled from high temperatures, but makes its appearance when such mixtures deposit solid. Only when the concentration of sulphur chloride was not more than 2% was it possible to demonstrate this distinction between two specimens of sulphur which had been treated in exactly the same way in respect to heating and chilling, but differed by the circumstance that in one case the separation of solid had been avoided and with it the production of S_μ. Nevertheless, the fact that the mere heating of sulphur and chilling does not by itself yield sulphur insoluble in carbon disulphide (or S_μ) was confirmed in numerous cases where solutions of sulphur in sulphur chloride and in other solvents, such as xylene, pyridine, and quinoline, were chilled from temperatures between 150° and 180° without solid separating and found to be completely miscible with carbon disulphide.

In the light of the above observations it becomes necessary to account for the insolubility in carbon disulphide of chilled sulphur by a hypothesis that does not postulate the pre-existence of the insoluble S_μ in the liquid from which it is produced on chilling, and we have therefore come to the conclusion that insoluble amorphous sulphur is probably a gel. The plasticity of freshly chilled sulphur obviously accords with this supposition; the " setting " of plastic sulphur to the hard amorphous S_μ is, we suggest, analogous to the hardening of gels such as those of hydrated oxides (silica gels, etc.). In further support of our view we adduce the following observations.

(i) *The solubility of* S_μ *in various solvents.* "Chilled" sulphur, prepared by distilling pure sulphur into cold water, was found to be insoluble in cold carbon disulphide, sulphur chloride, pyridine, quinoline, and xylene, whether it was in the rubber-like, plastic condition or had been kept until it had set to a hard mass. Rapid solution occurred, however, in the above solvents at temperatures above (roughly) 120°. For instance, 50% by weight of amorphous sulphur added to boiling sulphur chloride (138°) liquefied and dissolved completely in 5 seconds. A similar result was observed in quinoline at 130°; 10% of amorphous sulphur also dissolved readily and rapidly in liquid benzoic acid at 123°. In pyridine (b. p. 115°), dissolution was much slower and the amorphous sulphur did not liquefy completely: 10 g. dissolved completely, however, in 100 g. of solvent in 1 minute.

That amorphous sulphur (or S_μ) dissolves in hot solvents has, of course, long been known; but the fact that it does so has been ascribed to the effect of temperature in promoting its rapid change into soluble S_λ. It does not seem to be generally realised, however, that even at 140° it takes about 3 hours for "internal equilibrium" to be set up in liquid sulphur, and that "amorphous sulphur" kept at the natural f. p. of sulphur (114·5°) for 10 hours still contains 50% of insoluble sulphur (Smith and Carson, *loc. cit.*). Further, the authors (*loc. cit.*) found that in sulphur chloride solution at 148°, $1\frac{1}{2}$ hours were required to establish equilibrium. On the other hand, if S_μ is really a gel, it might be expected, like other gels such as rubber, gelatin, resins, etc., to show a more or less abrupt change in properties at and above the temperatures at which the gel structure is destroyed. It is significant that rapid dissolution of S_μ in solvents begins at about 120°, *i.e.*, at about the melting point of crystalline sulphur, which may possibly be the continuous phase in the gel.

(ii) *The Tyndall effect in liquid sulphur.* The hypothesis that chilled sulphur or S_μ is a gel led to the expectation that the liquid from which it is produced might show the properties of a sol. Liquid sulphur was therefore examined for the Tyndall effect. It is well known that the production of liquids in a state of optical purity is a matter of considerable difficulty. The sulphur used was therefore carefully purified by crystallisation from pure carbon disulphide and then by distillation, first under ordinary pressure and finally in a vacuum. It was then introduced into the side bulb of an apparatus of Pyrex glass, consisting of a cylindrical observation tube with flat top and bottom, the apparatus was exhausted with a mercury pump and sealed, and the sulphur distilled into the observation tube, remelted, and tipped back into the distillation bulb.* This was done six times, in order to wash out the observation tube, which was then surrounded by a small electric resistance furnace. A beam of light from a 500-watt lamp was focused through a window in the side of the furnace into the melted sulphur, which was observed through the top. A well-defined Tyndall beam of polarised scattered light was observed at all temperatures from the melting point up to 200°, at which the deep colour of the liquid sulphur prevented further observations.

Having obtained this characteristic indication of the presence of colloidal particles in liquid sulphur, we attempted to measure the intensity of the scattered light over a range of temperature in order to find out whether there was any correlation between the concentration of colloidal particles and the increase of viscosity of liquid sulphur that occurs at about 160°. The exciting beam was caused to enter the observation vessel as near to the bottom as possible, and at the same time light from a small electric-light bulb (3-watt) was passed vertically up through the base. By varying the resistance in circuit with the small bulb, it was possible roughly to match, by observation through the top of the tube, the intensity of the light transmitted from the control lamp through the liquid sulphur with the intensity of the Tyndall light. Both the direct and the scattered light had to traverse very nearly the same depth of liquid (about 8 cm.). The current flowing through the "control" lamp was measured on a milliammeter, and the temperature of the sulphur was varied by altering the resistance in series with the electric heating furnace that surrounded the observation tube. No great precision can be claimed for the observations made; nevertheless, the rather surprising conclusion can be drawn from them that, as far as could be detected by the rough apparatus used, no appreciable alteration in the intensity of the scattered Tyndall light could be observed between 125° and 200°. A typical series of measurements was :

Temp. of furnace ...	128°	135°	153°	165°	180°	200°
Current in control lamp (amp.) ...	0·45	0·43	0·435	0·45	0·44	0·45

Before these experiments could be repeated with more refined apparatus, however, a private communication from W. L. Cousins

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* In order to test this method for obtaining liquids optically "pure," experiments were carried out in similar pieces of apparatus with carbon tetrachloride and phenol. In each case two washings of the observation tube with distillate were sufficient to give liquids in which no Tyndall effect could be observed.

and B. Lange in Berlin informed us of results, to be published shortly, which they had obtained in measuring the intensity of polarisation of the Tyndall light in molten sulphur, and further work on the matter was abandoned.

In conclusion, it may be noted that the view that insoluble sulphur (S_μ) is a gel removes the difficulty in accounting for the fact that, although it is metastable with respect to crystalline sulphur, the latter is vastly more soluble.

Summary.

Experiments are described showing that insoluble sulphur (amorphous sulphur or S_μ) is not present as such in liquid sulphur but makes its appearance when the liquid solidifies. It is therefore suggested that S_μ is in reality a gel, and in support of this hypothesis its ready solubility in certain solvents at temperatures above the m. p. of crystalline sulphur (possible continuous phase) is noted, and the presence of colloidal particles in pure molten sulphur is established by observations on the Tyndall effect.

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