CCLXVII.—*Pseudo-ternary Systems containing Sulphur. Part I. Sulphur and Quinoline, Pyridine, and* p-*Xylene.*

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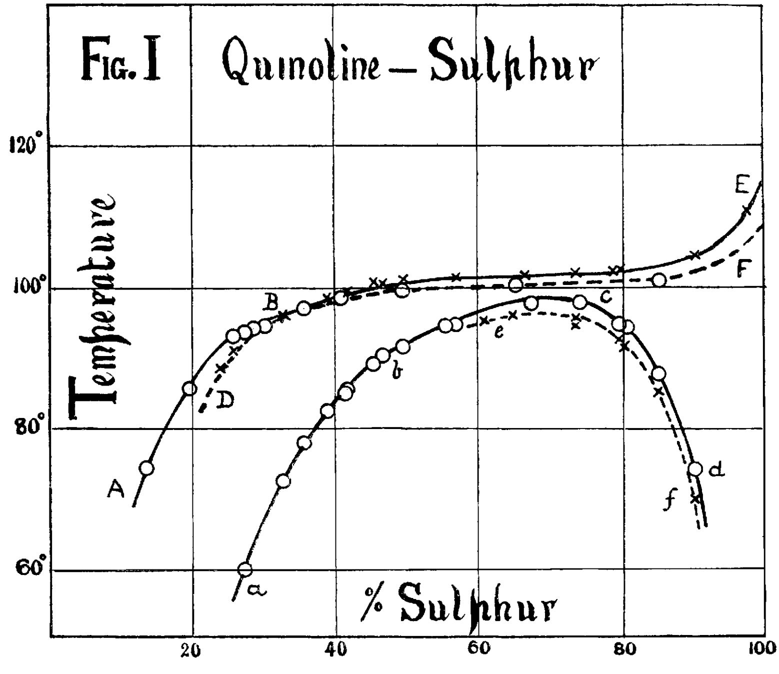
Equilibria in systems containing sulphur and an organic solvent have been studied by Smith (*J. Amer. Chem. Soc.*, 1905, **27**, 797) and by Kruyt (*Z. physikal. Chem.*, 1909, **65**, 496), who has discussed the forms of solubility curves to be expected in such systems. The experimental data, however, cover only certain ranges of concentration and temperature and, although they illustrate the possibilities predicted by Kruyt, they throw no light on the relationship between the stable, pseudo-ternary equilibria and the metastable equilibria to be obtained before equilibrium between S_λ and S_μ in the liquid phase is reached. A knowledge of this relationship is of importance in connexion with the results obtained by Äten (*Z. physikal. Chem.*, 1912, **81**, 257; 1913, **83**, 442; 1914, **86**, 1), in consequence of which he has inferred the existence of a new, very soluble form of sulphur, S_π. We have therefore investigated equilibria in the above systems by the synthetic method. As is well known, ammonia catalyses the rate of attainment of equilibrium between S_λ and S_μ and we expected that in the basic solvents pyridine and quinoline true pseudo-ternary equilibria would readily be attained. *p*-Xylene was chosen as being a non-polar solvent that could readily be obtained pure and in which the change from S_λ to S_μ might be expected to be sluggish.

The sulphur used was purified by two recrystallisations from toluene and was heated before use for several hours in a steamoven. Glass bulbs about 2 cm. in diameter were prepared with a neck about 10 cm. long. Weighed quantities of sulphur and solvent were introduced, the necks sealed off and drawn out to fine spindles. The tubes were then heated in a paraffin-bath, the temperature being slowly raised and the contents of the bulbs being agitated by frequent rapid rotation of the spindle. When temperatures had been reached at which the sulphur (solid or liquid) had almost disappeared, the bulbs were transferred to a thermostat, the temperature of which could be regulated to within 0·2°. By alternately raising and lowering the temperature and noticing whether the sulphur phase increased or diminished, it was possible to fix the equilibrium temperatures to within 0·3—0·5°.

FIG. 1.



The System Sulphur–Quinoline.

Synthetic quinoline (Poulenc Frères) was distilled and found to freeze at – 18·97° (mean of three determinations). Subsequent purification by freezing out twice (half the base being crystallised each time) gave a product with m. p. — 18·93° (Bramley, J., 1916, **109**, 472, gives — 19·5° as the m. p. of pure quinoline); consequently, freshly distilled quinoline was used without further purification.

In this system solid–liquid equilibria alone are stable. Points on the curve AB (Fig. 1) were obtained in the ordinary way using rhombic sulphur; the prolongation of AB to F was obtained by heating bulbs until a homogeneous phase was obtained and then either cooling rapidly to a few degrees below the temperature at which the expected solid phase should make its appearance or seeding with a trace of rhombic sulphur through a small hole in the neck of the bulb. The temperature of disappearance of the solid phase was then found in the usual way. BF thus represents metastable equilibria between rhombic sulphur and solutions. BE gives the stable equilibria between monoclinic sulphur and solutions, the metastable portion, BD, being obtained by rapid cooling as with BF. The data from which the curves ABF, DBE are plotted are in Tables I and II.

TABLE I.

Rhombic sulphur–quinoline.

% S by wt.	Temp. of equil.	% S by wt.	Temp. of equil.	% S by wt.	Temp. of equil.	% S by wt.	Temp. of equil.
13·8	74·5°	28·7	94·2°	32·95	96·0°	49·7	99·5°
19·8	85·8	30·4	94·6	41·9	98·5	65·3	100·0
25·9	93·2	32·8	96·5	49·5	99·5	85·2	101·0
*27·35	93·8						

TABLE II.

Monoclinic sulphur–quinoline.

% S by wt.	Temp. of equil.	% S by wt.	Temp. of equil.	% S by wt.	Temp. of equil.	% S by wt.	Temp. of equil.
24·0	88·75°	39·0	98·5°	49·5	101·1°	79·0	102·3°
25·9	91·0	41·9	99·2	57·0	101·4	79·8	102·5
32·8	96·0	*45·4	100·9	66·75	101·8	90·4	104·7
35·8	97·1	46·8	100·6	73·8	102·0	97·8	*111·5

The above equilibrium temperatures remained unchanged on keeping the sealed tubes; treatment of the contents of the bulbs with dry ammonia at about those temperatures also had no effect on the equilibrium temperatures. Thus the bulb corresponding to 27·35% of sulphur (marked *) in Table I was kept for 11 days, and the equilibrium temperature again found to be 93·8°. Also those marked * in Table II were kept for 17 and 13 days, respectively, and a stream of dry ammonia passed in for 20 minutes after they were opened. The bulbs were re-sealed and the temperatures of equilibrium found to be 100·9° and 111·5°.

Metastable Liquid–Liquid Equilibria.—When bulbs containing homogeneous mixtures at about 110° are cooled in the absence of solid phase, it usually happens that instead of crystalline sulphur separating, a new liquid phase appears. The temperature at which the cloud of droplets appears is sharply defined and usually does not differ by more than 0·4° from the temperature at which it disappears sharply on warming again. On keeping the bulbs at the temperature of disappearance, crystallisation would occur after times varying from minutes in some cases to hours in others. In Table III are the data plotted as the curve *abef* in Fig. 1; the equilibrium temperatures quoted are means of observed temperatures of separation and disappearance of the cloud of second liquid phase.

TABLE III.

% S.	*T.*	% S.	*T.*	% S.	*T.*	% S.	*T.*
27·35	60·0°	45·4	89·2°	57·0	94·8°	79·0	93·9°
32·8	72·6	46·8	90·2	60·9	95·2	79·8	92·6
35·8	78·0	49·5	91·6	65·3	96·0	80·5	91·9
39·0	82·5	49·7	91·6	66·3	95·5—96·2	85·2	85·4
41·5	85·0	55·4	94·3	66·75	96·5	90·4	70·0
41·9	85·5	55·5	94·5	73·8	94·8		

Mixtures containing less than 50% of sulphur were unaffected by heating for several hours at 90° or by keeping for several weeks at room temperature. When mixtures containing more than 50% of sulphur are treated in this way, the temperature of separation slowly rises, a final temperature being reached that remains unchanged on further heating and keeping. These final values are plotted as the curve *cd* and are given in Table IV.

TABLE IV.

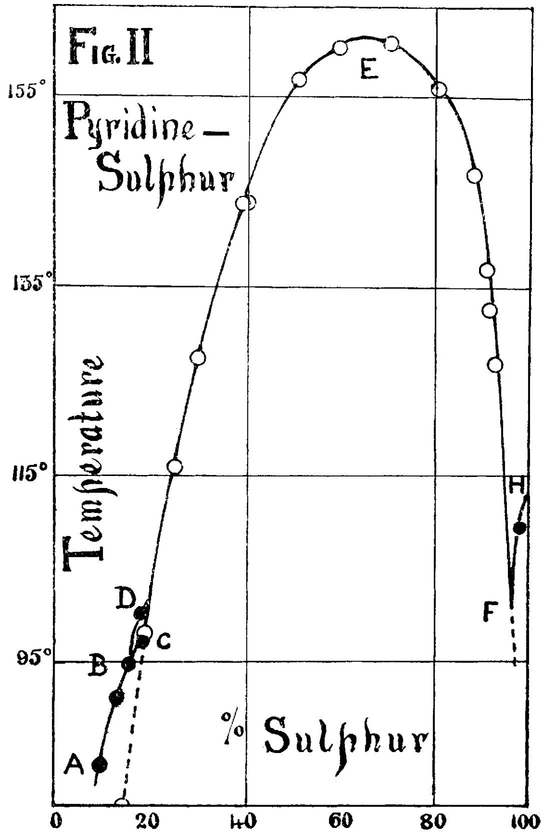
% S	49·5	49·7	66·75	73·8	79·8	80·5	85·2	90·4
T °	91·8	91·8	97·5	97·6	94·6	94·3	87·7	72·0

The curve *abcd* thus represents true (metastable) pseudo-ternary equilibria, corresponding to sulphur present as an equilibrium mixture of its various molecular species. The lower curve *ef* refers to a labile, binary system, presumably S_λ–quinoline.

In order to test this view, attempts were made to estimate the amounts of S_μ present before and after internal equilibrium had been reached. Two bulbs were brought to the states represented by points on the curve *ef* and two to points on the curve *bcd*. They were then broken under a mixture of hydrochloric acid and ice, the sulphur and glass filtered off, dried and extracted with carbon disulphide. The insoluble S_μ and glass were collected and weighed together, the glass being finally weighed after the sulphur had been burned away. No weighable amount of S_μ was obtained from either of the bulbs containing labile sulphur (curve *ef*); the sulphur in the other two bulbs (curve *abcd*) contained 1·4 and 1·6% S_μ respectively.

It would thus appear that the curve *ef* represents systems in which internal equilibrium between S_λ and S_μ has not been reached. The solid–liquid systems are almost certainly pseudo-ternary, for points on the curves took several hours to determine and were unchanged after keeping the bulbs for weeks. In fact, it is rather remarkable that with a basic solvent such as quinoline any information at all could be obtained about the labile binary system.

FIG. 2.



The System Pyridine–Sulphur.

The pyridine boiled between 114·8 and 115·3°. Equilibria were determined as in the case of quinoline, except that for temperatures above 150° a regulated air-oven was used as a thermostat. The results in Tables V and VI were obtained and are plotted in Fig. 2.

TABLE V.

Solid–Liquid Equilibria.

% S	10·05	13·35	15·9	16·9	19·2	98·0
Solution temp. (rhombic)...........	84·5°	91·5°	95·2°	97·5°	—	—
,, ,, (monoclinic)	—	—	—	—	101·0°	110·0°

These points are shown as black dots in the figure, on the curves ABC, BD, and FH.

TABLE VI.

Liquid–Liquid Equilibria.

% S.	*T.*	% S.	*T.*	% S.	*T.*	% S.	*T.*
13·35	*ca.* 80°	38·6	144·0°	70·0	161·0°	88·4	132·5°
19·2	98·0	38·9	144·0	79·7	156·0	90·0	137·0
24·65	116·0	50·7	157·0	87·78	147·0	91·94	127·0
29·8	127·5	59·0	160·5				

These data are plotted as the curve CEF.

Several of the sulphur–pyridine mixtures were kept at the temperature of equilibrium for some hours without appreciable alteration of the equilibrium temperatures; no indication of a second liquid phase was obtained when the bulbs containing 59% and 70% of sulphur were heated to about 200°.

*The System Sulphur–*p*-Xylene.*

The *p*-xylene used was purified by freezing out and melted at 13·2°. Equilibria were determined as in the other systems.

TABLE VII.

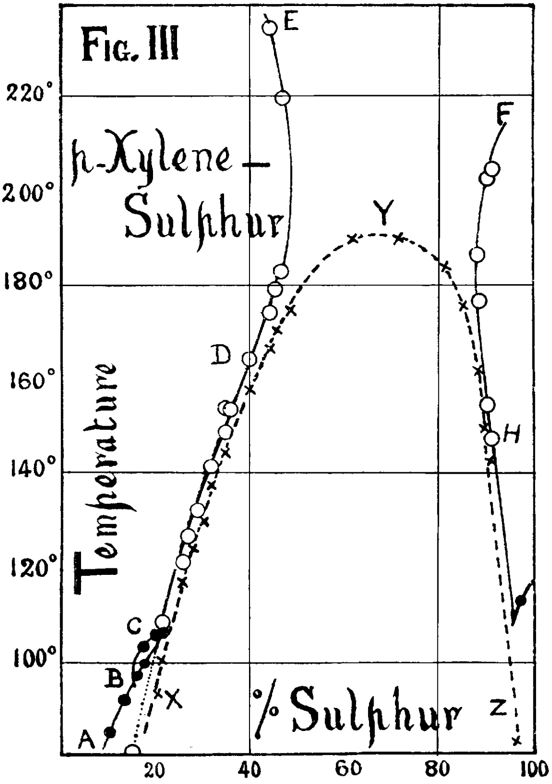
Solid–Liquid Equilibria.

% S	21·8	16·25	13·95	16·3	20·38	17·85	11·0
Equil. temp. (rhombic)	—	—	92·5°	—	—	100·5°	85·0°
,, ,, (monoclinic) ...	107·0°	98·2°	—	98·0°	106·0°	103·3°	—

These results are in Table VII and are plotted in Fig. 3 as the curves AB (rhombic) and BC (monoclinic).

Liquid–Liquid Equilibria.—Temperatures of complete solution found by examining freshly prepared bulbs are plotted as the curve XYZ. The paraffin-bath was stirred and heated in such a way that its temperature rose at the rate of about 2° per minute when it was about 10° below the temperature at which complete solution was expected. When bulbs were placed in the heating bath and rapidly rotated, the heterogeneous contents cleared sharply at points on the curve XYZ; these points were fixed as the means of observations made with rising and falling temperatures which did not differ by more than 1°. On keeping a bulb for a few minutes, however, under conditions represented by a point on XYZ, the clear solution becomes cloudy owing to the reseparation of a second liquid phase and the temperature of complete solution rises until it becomes constant, after times varying from ½-hour in the case of bulbs corresponding to higher portions of the curve XYZ to a few hours in the case of those corresponding to the lower portions. These higher steady temperatures of complete solution when plotted give the curves CDE, HF. Points on the retrograde portions of the curves CDE, HF were obtained by raising the temperature of mixtures that had become homogeneous until a new liquid phase separated.

FIG. 3.



Below about 140° the liquid phase separates in the form of fairly large drops; above 140° the cloud is composed of much smaller droplets and disappears much more sharply on raising the temperature. This fact has its effect on the experimental error, which varies from ± 1° in the lower portions of the curves to about ± 0·5° in the middle portions of the range 140—150°.

The results obtained are in Table VIII; col. 2 gives temperatures (T_1) at which the second liquid phase first dissolves; col. 3 contains the temperatures (T_2) at which the second phase finally dissolves after keeping; col. 4 gives the temperatures (T_3) at which mixtures that have become homogeneous at lower temperatures again separate into two liquid layers.

TABLE VIII.

% S by wt.	T_1.	T_2.	T_3.	% S by wt.	T_1.	T_2.	T_3.
16·25		*ca.* 80°		44·1	167·5°	174·5°	
20·38	94·0°			45·7	171·0	179·5	
21·8	101·0	109·0		46·3	175·0	183·5	220·0
25·9	117·7	121·7					
27·8		127·0					
27·95	124·5	129·2		48·3	175·0	Approx. equal cloudiness at 196·0 and 206·0	
28·04	124·2			61·7	190·0		
29·1		132·0		71·2	190·0		
30·22	130·0	133·7		81·0	184·0		
31·95	137·3	141·5		85·6	176·0		
34·6	144·5	148·25		85·5	156·0		
34·9	149·0	150·0		87·9	162·5	177·0	187·0
36·0		154·0		90·0	150·0	155·0	203·0
39·9	158·5	165·0		91·0	143·0	147·5	205·0
44·0	167·0	174·5	235·0°	96·2		84·0	

Discussion.

It has been shown that in the systems quinoline–sulphur and *p*-xylene–sulphur the attainment of internal equilibria in the phases containing liquid sulphur results in a lowering of the mutual miscibility of those phases. This effect is shown particularly well in the *p*-xylene system, in which it has been possible to determine liquid solubilities over a wide range of temperatures before and after internal equilibrium had been reached in the sulphur.

According to Äten (*loc. cit.*), liquid sulphur in internal equilibrium contains three molecular species, S_λ, S_μ and S_π, S_μ being very insoluble and S_π more soluble than S_λ. Äten gives a table of the percentages of the three forms present in molten sulphur at temperatures from 120° to 445° (*Z. physikal. Chem.*, 1913, **86**, 1). According to this, the amount of S_π present does not vary much from about 5% over the whole temperature range; S_μ, however, is present to the extent of 0·1% at 120° and increases to 1·6% at 145°. As the inflexion point in the Smith and Carson allelotropic curve for liquid sulphur is approached, the amount of S_μ increases rapidly, being 4·1% at 160° and 13·3% at 170°. On the basis of these figures we should expect, unless the internal equilibrium is very profoundly modified by the presence of the solvent *p*-xylene, that the solubility of equilibrium sulphur would exceed that of S_λ at lower temperatures. At higher temperatures, as the percentage of S_μ

increases rapidly, equilibrium sulphur should become less soluble than S_λ. These conclusions are not borne out by the results given above for the system sulphur–*p*-xylene, in which, over the whole temperature range investigated, the solubility of the liquid equilibrium sulphur is definitely less than that of the labile S_λ.

According to the views on the mutual miscibility of liquids developed by Hildebrand (*J. Amer. Chem. Soc.*, 1916, **38**, 1452; 1919, **41**, 1957; 1921, **43**, 500; etc.), non-polar liquids are incompletely miscible only when their internal pressures differ considerably and the greater the difference the higher is the critical solution temperature for the two liquids. Although it is not possible to determine values for internal pressures with any certainty, it is highly probable that they stand for xylene, toluene, and benzene in the order named (Hildebrand, *loc. cit.*). Judging from the values for the surface tension and latent heat of sulphur, its internal pressure is very much greater than those of the aromatic hydrocarbons. We should expect, therefore, that the critical solution temperatures of sulphur in the above solvents should descend in the order xylene, toluene, benzene. From Fig. 3 it appears that the critical solution temperature in xylene is 190° for S_λ; Kruyt (*loc. cit.*) found 180° in toluene and 160° in benzene for equilibrium sulphur.

Again according to Hildebrand, if one of the liquids in a binary mixture is polar (having a high value for its dielectric constant), the effect of this polarity is to diminish the mutual solubility. This conclusion receives support from the results of our experiments on the systems sulphur–pyridine and sulphur–quinoline; these are in Table IX, which includes the result of an experiment in which a mixture of alcohol and sulphur was heated in a sealed tube to above 170° without complete solution taking place.

TABLE IX.

	Diel. const.	Crit. sol. temp.
Quinoline	9·8	97°
Pyridine	12·4	160
Ethyl alcohol	26·0	>170

The internal pressures of the above three solvents are of the same order and very much less than that of sulphur.

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