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ON AMORPHOUS SULPHUR: II. ON TWO LIQUID STATES OF AGGREGATION OF SULPHUR, S_λ AND S_μ, AND THEIR TRANSITION POINT.[1]

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When common sulphur is raised to a high temperature and then allowed to cool slowly, the whole of the product is crystalline and completely soluble in carbon disulphide. If the specimen of heated sulphur is chilled suddenly, however, it is a familiar fact that a larger or smaller proportion of the material, after it has hardened, is amorphous and insoluble. In a preliminary paper[2] the authors have shown that when carbon dioxide, or better still ammonia, is led for a few minutes through the molten sulphur no insoluble sulphur is found after chilling. The resulting crystalline sulphur, if used at once, may be heated to the boiling-point, or any lower temperature, and chilled without the production of any amorphous sulphur. Sulphur dioxide, however, restores the

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[1] Presented in abstract at the Philadelphia Meeting (Dec., 1904) of the American Chemical Society. The first paper of this series, "On Amorphous Sulphur: I. The Relation of Amorphous Sulphur to the Freezing-point of Liquid Sulphur," appeared in the Decennial Publications of the University of Chicago, Vol. IX, p. 55. It was published also in *Z. physik. Chem.*, **42**, 469 (1903).

[2] *Ber.*, **35**, 2992 (1902). In a paper following the present one, No. III, a more complete series of experiments on supercooling will be communicated and in it the relation of the insoluble sulphur to the phenomena described in the present paper is determined

capacity to give insoluble sulphur. When the treatments are used alternately, the result is determined by the last of the two gases which has been employed. Sulphur used immediately after recrystallization also yields no insoluble sulphur. In the course of the further investigation of this phenomenon the question arose: Whether the ammonia, for example, actually destroyed and removed the insoluble sulphur which was in solution in the liquid soluble sulphur, or whether it simply altered the behavior of the former so that it reverted to soluble sulphur more rapidly and thus disappeared during even the most rapid chilling. The present investigation was originally undertaken as one means of securing light on this point. The bearing of the subject of this paper upon the point in question was briefly as follows: It had been shown in the first paper of this series[1] that the freezing-point of soluble sulphur is depressed by insoluble sulphur in accordance with Raoult's law. It was therefore to be expected that this substance would also displace another transition point, of which there was reason to suspect the existence in melted sulphur in the neighborhood of 160-170°. If therefore this transition point should be found to exist, and if two kinds of specimens, which when chilled respectively did and did not yield insoluble sulphur, should be found to give *different* values for the temperature of the transition, the actual destructon of the dissolved insoluble sulphur might reasonably be inferred. If, on the contrary, all specimens showed the *same* transition point, then the same proportion of insoluble sulphur was present in both kinds at that temperature and the seeming destruction was due to rapid reversion during the supercooling. The results, which are described below, showed that a sharp transition point did exist, and that in all specimens it occurred at precisely the same temperature.

I. THE PRESUMED TRANSITION POINT.

Introductory.—It is well known that sulphur melts at about 115°, giving a pale yellow, mobile liquid and that between 160° and 170° it becomes deep brown in color and suffers a rather sudden access of extreme viscosity. Berthelot[2] supercooled sulphur at various temperatures and estimated the amount of insoluble sulphur. He found that almost none of this form was obtainable below 170° while 25-30 per cent. was always secured

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[1] *Proc. Roy. Soc.* (Edin.), **24**, 299 (1902): *Z. phys. Chem.*, **42**, 469 (1903).

[2] *Ann. ch. ph.* (3), **49**, 476 (1857).

from specimens which had reached higher temperatures. Special means of chilling enabled him to increase the yield. He inferred therefore that at 171° the whole of the sulphur was transformed into insoluble sulphur and that the sudden thickening of the liquid coincided with this change. More exact measurements,[1] made by the same procedure, showed us that there were considerable and continuously increasing quantities of insoluble sulphur in sulphur even below 170° and demonstrated that Berthelot's method of experiment was not capable of giving results to justify his conclusion. Furthermore, sulphur treated with ammonia, and so bereft of the capacity to yield insoluble sulphur, still became thick at 170°, so that the existence of an intimate connection between the viscosity and the content of insoluble sulphur was also, for a time, in doubt.

Careful measurements of the variation in the viscosity with change in temperature, made by Brunhes and Dussey,[2] indicate that the mobility of the liquid increases from 115° to 156-157° in the ratio 5:9. From this point the mobility diminishes very rapidly. At 162° the liquid is extremely viscous and at 180° the minimum of mobility is reached.

Frankenheim[3] seems to have been the first and only observer to offer an explanation of the viscosity. From a study of the irregularities in the rate at which constantly heated sulphur rises in temperature he concludes that there is one, and only one point at which a definite absorpton of heat always occurs. This is at 260°. He infers that a transformation into a new liquid state takes place at this point. He explains the extreme viscosity from 170-260° by the theory that the separation of the new liquid begins at 170° and goes on throughout this whole region of temperature. In such circumstances the mass is an emulsion of minute droplets of two liquids and owes its viscosity to the ascendency of the surface properties over those natural to either liquid in its separate condition.

Considerations based upon the phase rule make it easy to test this hypothesis. One substance cannot exist in three phases (two liquid and one vapor phase) except as a non-variant system at a single temperature and pressure. It is evident therefore that an

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[1] The results will be given in another paper.

[2] *Compt. Rend.*, **118**, 1045 (1891).

[3] *J. prakt. Chem.*, **16**, 5 (1839).

extended region of stable coexistence for two liquid forms is impossible. On the other hand, many facts show that a state of unstable equilibrium cannot persist in sulphur at 170-180° for more than a few minutes. To test the above hypothesis we therefore kept a specimen of sulphur at 180° constantly for several days. Since during this time no diminution in the viscosity was perceptible, we inferred that great viscosity is a specific property of sulphur at that temperature.

Several other facts, to be mentioned later, were also known when this work began, and these indicated some temperature below 170° as the probable transition point.

Although the existence of two states of a liquid has not previously been established in any perfectly simple case, yet the sharp transition of "crystalline liquids"[1] to isotropic liquids is to a certain extent parallel to what we expected to find. It is true that the peculiar organic compounds which show such a transition melt first to give "liquid crystals" which are optically active, while liquid sulphur is found to be isotropic at all temperatures, so that in this respect the analogy fails. There is, however, no necessity for believing that some special mode of orientation of, or in, the molecules is a condition essential to the existence of a distinct liquid form. A certain degree of mutual insolubility would be sufficient to cause the separation of a new phase and would lead to the appearance of a transition point. That one form of sulphur—the amorphous form—could exist in solution in another form—the soluble one—and behave in all respects like a foreign solute was shown by the fact that it depressed the freezing-point of the material.[2] Since two liquid states of the same substance are not likely to be completely immiscible, it is to be expected that a certain amount of the liquid form which predominates above the transition point (S_μ) will be formed below this point and will exist in solution in equilibrium with the other liquid ($S\lambda$). The transition will then be determined by the fact that the liquid proper to the lower temperatures has at length become saturated with S_μ. This will then separate, as from a supersaturated solution, and the new phase will then contain some

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[1] Shown by cholestryl benzoate (Reinitzer: *Monatshefte*, **9**, 435) and by *p*-azoxyphenetol and *p*-azoxyanisol (Gattermann: *Ber.*, **23**, 1738). For a physico-chemical study of these cases see Schenck: *Z. phys. Chem.*, **23**, 703; **25**, 337; **25**, 349; **27**, 167; **28**, 280; **29**, 546; Hulett: *Ibid.*, **28**, 629.

[2] Smith and Holmes: *Z. phys. Chem.*, **42**, 469.

of the liquid proper to the lower temperatures (S_λ) as a solute in S_μ. The S_λ will then gradually become less in amount as the temperature rises.

The Methods Used.—There are several methods which should be available for ascertaining definitely whether a transition point exists, and for determining its exact location. When such a point occurs there must be a sharp discontinuity at the transition temperature in the rate at which every physical property changes with temperature. Curves representing viscosity, dilatation, solubility, vapor-tension, refractive index, etc., must all take a new direction at this point. We employed the first three of these properties. At such a point, also, as at the melting-point of a solid, an absorption of heat should be observed, and this was found to be the case with sulphur. By these means it was shown that a transition does occur and that it takes place at 160°. We have designated the liquid forms S_λ and S_μ. The former is the predominating substance up to 160° and the latter for an undetermined distance beyond this temperature. With the exception of one set of observations at 220-266°, no attempt has yet been made to explore the region above 160°.

II. CHANGE IN MOBILITY AT THE TRANSITION POINT.

Object of the Experiments.—The measurements of Brunhes and Dussey placed the onset of the viscosity at 156-157°. Their results may be accepted in spite of the fact that our observations place the transition at 160°. It is to be expected that the two liquid forms of sulphur will be somewhat miscible and that therefore the S_μ dissolved in the S_λ will lead to a perceptible increase in the viscosity of the latter below the temperature at which the transition actually takes place. In this connection, therefore, our only task was to ascertain whether or not sulphur treated with ammonia, and incapable of giving insoluble sulphur, shows the same behavior as ordinary sulphur. We had observed previously[1] that such sulphur does become viscous. It remained only to ascertain whether it did so at the same or at a different temperature.

Experimental Method.—Preliminary experiments proved that it was easy, by too rapid heating, to overshoot the minimum temperature at which the viscosity could appear. This was to be expected, since supersaturation of the S_λ with S_μ might readily

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[1] *Ber.*, **35**, 2993.

occur and the separation of the new phase be postponed to a higher temperature. A method of raising the temperature very slowly and in an easily controllable fashion was necessary in order that there might be time for a continuous adjustment of the material to the state of equilibrium proper to each temperature. A bath of α-dichlorhydrin (b. p. 174°) boiling under reduced pressure was therefore employed for heating. Its temperature was altered by changing, a very little at a time, the pressure under which it boiled[1]. In the neighborhood of the transition point the temperature was not allowed to rise faster than 1° per hour. The apparatus consisted of an outer tube such as is used in V. Meyer's method for measuring vapor-density. This contained the dichlorhydrin. An inner tube contained melted paraffin, the presence of which enabled us to secure a steady rise in the temperature of the sulphur in spite of the slightly discontinuous nature of the changes in the temperature of the vapor-bath. The tube containing the sulphur stood in the paraffin. It was not, as with Brunhes and Dussey, our purpose to observe the point of maximum mobility, but to find a point a little above this at which a noteworthy degree of viscosity had appeared. By means of a fine platinum wire with a loop at the end the first appearance of such viscosity could easily be ascertained within 0.5° or less. At 159° the sulphur appeared, by this means of observation, to be as mobile as at 120°; at 160° it was so thick that the wire sank with difficulty. This degree of accuracy was sufficient for our purpose, since it was here simply a question of whether or not 12 per cent. of a foreign substance was present.[2]

Pure recrystallized rhombic sulphur which had been kept in the laboratory for months was used.

Results.—The temperatures at which viscosity first became perceptible were as follows:

Ordinary sulphur, 159.5°; 159.7°; 159.1°. Mean, 159.4°.

Sulphur treated with ammonia, 159.5°; 159.5°; Mean, 159.5°.

Ordinary sulphur chilled from 160° gives 11 per cent. of insoluble sulphur. To make certain that no error had been committed,

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[1] Ramsay and Young: *J. Chem. Soc.*, **47**, 640 (1885). A large vacuum-reservoir and automatic pressure-regulator made possible the maintenance of any required temperature for any length of time.

[2] An experiment described later enabled us to calculate, roughly, that the presence or absence of this amount of a body of molecular weight S_8 (*Z. phys. Chem.*, **42**, 479) should have made a difference of 36° in the transition point.

one of the specimens of sulphur treated with ammonia was chilled and was found to give on extraction no insoluble sulphur whatever.

The experiments in this and the following sections were all repeated with distilled sulphur, because its behavior was always somewhat different from that of crystallized sulphur. It appeared to be much more liable to become superheated. Thus, with it, no viscosity could be observed at 160°, even when the fluid was kept for half an hour at this temperature. The viscosity appeared first at 161.5-162° and even then asserted itself rather gradually. While no cases of superheating a solid are known, the superheating and supercooling of liquids are both familiar. Hence no doubt was felt in regard to the correctness of this explanation.

III. HEAT ABSORPTION AT THE TRANSITION POINT.

Previous Observations.—Marx[1] was the first to observe irregularities in the rates of heating and of cooling in sulphur. Frankenheim[2] found that specimens submitted to different rates of heating, and even different specimens heated in the same way, behaved differently. He attributed all the irregularities, save a noticeable one at 250-260°, to unequal heating or cooling due to changes in viscosity. At 250-260°, with rising temperature, a marked absorption of heat was shown by all specimens. On cooling, a development of heat at this point caused a delay in the fall in temperature. Deville,[3] on the other hand, found the behavior at 250-260° normal; but he believed he had evidence, as the temperature rose, of an evolution of heat at 120-160° and again between 180-230°. In cooling there was a slight evolution of heat at 240-210°, an absorption at 180-160°, possibly a slight evolution at 160-145°, and an absorption at 145-135°. He considered the release of heat between 240° and 210° as the only significant part of the phenomena and related it to the fact that the greatest viscosity existed between these temperatures. Schaum[4] found that sulphur standing in a bath of constantly rising temperature showed a notable absorption of heat, indicated by a sudden drop in temperature, near 168°. Thus on different occasions the thermometer fell from 168.0° to 166.3°, from 168.6°

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[1] *Schweigg.*, **60**, 1 (1830).

[2] *J. prakt. Chem.*, **16**, 7 (1839).

[3] *Ann. ch. ph.* (3), **47**, 94 (1846).

[4] *Ann. Chem.* (Liebig), **308**, 25 (1899).

to 166.8° and from 167.8° to 166.8°, before beginning to reascend.

In none of these cases is any mention made of an attempt to avoid unequal heating by the use of stirring apparatus.

The Need of Stirring.—The eccentricities in behavior when stirring is not employed were illustrated strikingly in our first experiments by this method. Thus the readings of the thermometer at intervals of one minute, during part of one experiment, were as follows: On heating: 157.5°; 160°; 162°; 164°; 166°; 167°.5; 166.5°; 168°; 170°; 172°. In cooling: 175.5°; 172°; 168.5°; 164.5°; 159.5°; 145°; 138.5°; 134°; 129.5°. As the temperature rose, the ascent from 164° to 166° took one minute, while that from 167.5° to 168° took two minutes. As the temperature fell the descent at 168.5 was 4° per minute, and at 159.5° it was 14.5°. In other words, heat appeared to be absorbed near 160-170° both in ascending and in descending, a result in conflict with the laws of energy! The cause of the sudden drop in temperature as the thermometer fell was traced to the adhesion of a mass of viscous, poorly conducting sulphur to the bulb of the instrument and its sudden displacement by the mobile and cooler sulphur from the layers which, being nearer to the sides of the tube, had lost heat more rapidly by radiation.

The Tendency to Various Degrees of Superheating.—Even when the sulphur was stirred vigorously, however, the temperatures at which absorption of heat was observed with ascending temperature were different with every experiment. Thus specimens of ordinary melted rhombic sulphur showed it at 169°, 167°, and 170.5° according to the rate of heating. Similar specimens treated with ammonia gave slighter evidence of the absorption and the temperatures were sometimes lower: 160-162°, 167.5°, 161°. Specimens specially recrystallized from other solvents than carbon disulphide gave more marked effects. The solvents used and the points at which the absorption of heat was observed were as follows: Chloroform, 176° (fell to 171.5°); toluene, 183° (fell to 177.8°). Sulphur twice distilled and then recrystallized from carbon disulphide fell from 179° to 174.5°. Distilled sulphur showed either no interruption whatever in the steadiness of the rise in temperature, or at most a very slight one.

In all cases in which any evidence of absorption of heat was noticed, the sulphur became suddenly viscous at the same moment. With the distilled sulphur the viscosity appeared more gradually.

It was evident that with this method of experiment, in which there was a rapid ascent of the temperature, the various specimens of sulphur suffered superheating in various degrees and the observations were of no value except as evidence of the fact that small traces of impurities had a great effect upon the facility with which superheating occurred.

The Minimum Temperature at which Heat Absorption Could Be Observed.—To avoid overshooting of the transition point caused by the rapid rate at which the temperature rose, a bath was arranged so that its temperature could be maintained at some fixed point. The sulphur contained in a tube was placed in this bath and vigorously stirred. Thermometers in the bath and in the sulphur enabled the temperature of each to be read. It was found that when the sulphur, prepared by melting the crystalline material, was kept for a sufficient length of time at 162.5° or any higher temperature, a sudden fall, accompanied by thickening, ultimately set in. Often half an hour elapsed before the drop in temperature was observed. When the sulphur was held at temperatures lower than 162.5°, no fall in temperature occurred. On only one occasion did the temperature fall so low as 161.5°, in the other cases it fell to 162°. Sulphur recrystallized from toluene showed the effect very sharply, the temperature remaining for fifteen minutes at 163° and then suddenly falling to 162°. Distilled sulphur, however, could not be made to show any evidence of heat absorption at 163° and became viscous gradually at this temperature. Inoculation with brown viscous sulphur had no decided effect in any of the experiments.

Sulphur, prepared by melting crystalline sulphur, behaved after treatment with ammonia, exactly like that which had not been so treated.

The experiments made by this method could not give the exact transition point, but the results showed that the point was certainly below 162°. They demonstrated also that for different specimens of sulphur the position of the point was the same, whether the specimens were such as, when chilled, give insoluble sulphur or not.

IV. THE SOLUBILITIES OF THE TWO LIQUID FORMS OF SULPHUR.

Preliminary Experiments.—It was expected that the two liquid forms of sulphur would show different curves of solubility in the same solvent. The very first experiments gave even more striking evidence of this than had been hoped. Sulphur was found to dissolve freely in melted diphenylmethane, diphenyl, β-naphthol, and triphenylmethane, and that with little or no evidence of chemical interaction even at 200°. In these substances sulphur seemed to be very soluble at about 170°. In each case, when the solution was allowed to cool to the saturation point, liquid sulphur separated. In each case, when the temperature was once more raised, the emulsion first became clear and then at a much higher temperature (above 170°) liquid sulphur began to separate once more. Thus with 18 grams of sulphur and 10 grams of triphenylmethane the separations occurred at 147° and at 214.5°.

Since the *same* substance cannot be in equilibrium with solutions of the same concentration at two different temperatures it follows that either the dissolved sulphur underwent a change, or the sulphurs which were deposited and remained in contact with the solution were different. In each case, the sulphur which separated on cooling was pale yellow and mobile, while that which separated on heating was deep brown and viscous. It appeared therefore that it was the sulphur phase which was different. In view of van't Hoff's law, it was further evident that $S\lambda$ dissolved in these solvents with absorption of heat and should show an ascending curve of solubility, and that $S\mu$ dissolved with evolution of heat and should show a descending curve of solubility.

The sulphur phase which appeared was, of course, in each case a solution of the solvent in sulphur and not pure sulphur. A sudden clouding of the sulphur phase itself, which occurred when it was allowed to cool, was due to the formation of a new phase consisting mainly of the original solvent.

We were unable to find any solvent for which the solubility could be measured throughout the whole range from 110° to 210°, without the occurrence of complete miscibility near to 160-170°. The intersection of the two curves, therefore, could not be observed. Hence these experiments demonstrate only the absolutely different nature of the two liquids and do not lead to a measurement of the transition point. This is a matter of small moment however, because the point of intersection, if found, would be the one at which the solution is in equilibrium with two solutions of the solvent in sulphur, and not with two pure forms of sulphur. The temperature of the intersection might, therefore, be far removed from the transition point.

The Method and Results of Solubility Measurements.—For measuring the solubilities the synthetic method was used. A weighed quantity of the organic solvent was taken and to it was added a weighed quantity of sulphur. The mixture having been heated by means of a bath of melted paraffin until it was clear and homogeneous, the flame was removed and the temperature at which clouding began was taken. After verification of this point, an additional known quantity of sulphur was thrown in and the process repeated. The points of saturation at the higher temperatures were obtained in corresponding fashion. Pure recrystallized sulphur was used. The results were as follows:

Triphenylmethane.—The saturation points for S_λ, at lower temperatures, are on the left, those for S_μ on the right. The first column (S) gives, in each case, the proportion of sulphur to 10 grams of triphenylmethane; the second column (t), the temperatures of clouding.

S_λ.		S_μ.	
S.	t.	S.	t.
4.47	108.5	18.20	214.5
5.48	117.0	20.74	211.0
7.02	127.0	25.15	206.0
8.09	131.0	30.89	203.0
9.68	136.5	36.29	200.0
11.46	141.0	42.19	199.0
13.37	144.0	54.85	198.0
16.45	146.0		
19.68	146.5		
23.04	147.0		
29.33	146.0		

The curves are shown in Fig. 1, in which the temperatures are laid off horizontally and the concentrations vertically. The last observation (146°) on the lower curve is on the upper branch of this curve and in this experiment, as is to be expected, it was triphenylmethane which separated and not sulphur.

β-Naphthol.—With this substance two series of measurements of the lower saturation points were made. In the first (I) ordinary crystallized sulphur was used, in the other (II) sulphur which had been treated with ammonia[1]. No observations of the

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[1] In the latter case, however, when the solution was suddenly chilled from 163°, after the measurements had been completed, 4.3 per cent. of insoluble sulphur was found in the product (see next paper, section. 7).

higher saturation points (above 200°) were made, as there was some chemical interaction.

I.		II.	
s.	t.	s.	t.
3.40	118.0	4.88	134.5
4.66	132.5	9.74	157.0
5.93	143.5	11.93	160.5
7.00	149.5	14.51	162.5
8.41	154.0	17.76	163.5
(Tube broken		20.97	164.0
and series		23.81	163.8
interrupted.)		26.48	163.8
		30.00	163.0

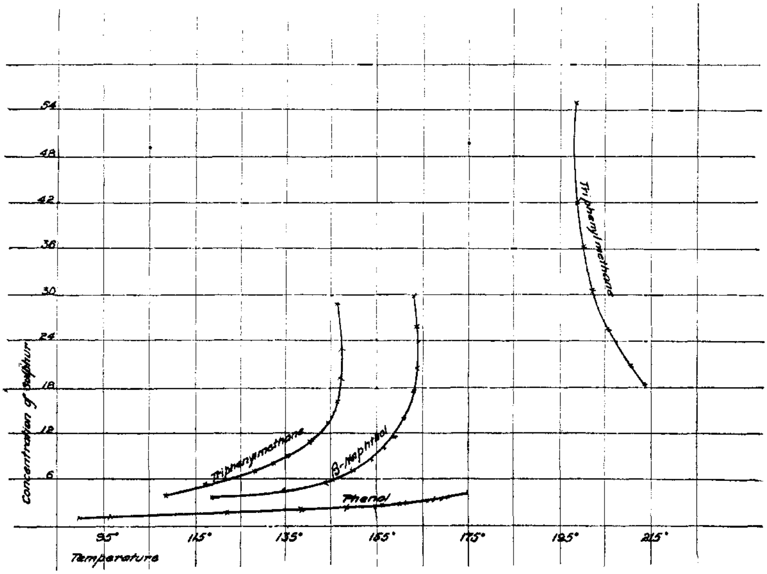

Fig. 1.

The last two observations of the second set showed separation of β-naphthol, and lie upon the upper branch of the curve (Fig. 1).

Phenol.—The series with phenol was naturally limited to the region below the boiling-point (183°) of the organic compound. Sulphur which had been melted and treated with ammonia was used.[1]

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[1] When the homogeneous solution, containing 27 per cent. of dissolved sulphur, was suddenly chilled from above 175°, 4.84 per cent. of insoluble sulphur was found in the residue.

S.	t.	S.	t.
0.91	89.5	2.96	162.0
1.04	96.5	3.07	164.5
1.53	122.5	3.16	166.0
1.99	138.0	3.24	167.5
2.36	148.5	3.35	170.0
2.63	155.0	3.49	172.0
2.71	157.5	3.65	175.0
2.86	160.5		

The curve derived from these results (Fig. 1) shows no break although the maximum temperature is considerably above the transition point. The experiments to be described in the next section, however, show that the transition point is greatly raised by the presence of a dissolved body in the sulphur, so that the transition point of sulphur saturated with phenol may be considerably above even the highest temperature (175°) here attained.

In the effort to secure continuous measurements extending past the transition point, several series of observations were made, using solutions of sulphur in triphenylmethane with which various proportions of phenol had been mixed. It was hoped thus to reduce the solubility values, which, with triphenylmethane, are extremely high. In these experiments a point as high as 180.5° was reached without any break in the curve being encountered. Only one observation from these sets will be given. It was one in which the double separation of sulphur appeared. With 2.5 grams phenol, 7.5 grams triphenylmethane and 25.36 grams sulphur, separation of sulphur occurred at 158.5° and again at 208.5°.

V. DILATOMETRIC STUDY OF THE TRANSITION POINT.

Previous Measurements.—The only complete series of measurements of the coefficient of expansion of sulphur from 110° to the boiling-point was made by Moitessier[1]. The values he found were as follows:

110–120°	0.000551	225–250°	0.000338
120–140°	0.000490	250–275°	0.000358
140–160°	0.000380	275–300°	0.000374
160–180°	0.000210	300–350°	0.000401
180–200°	0.000262	350–400°	0.000437
200–225°	0.000320	400–440°	0.000469

These figures show a very sharp descent to 160-180° and a rapid ascent beyond it. When they are plotted, the curve is V-shaped

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[1] *Mem. Acad. de Montpellier*, **6**, 107 (1864).

with the minimum exactly at 170°. Moitessier attributed the diminution in the coefficient to the formation of increasing amounts of insoluble sulphur. Presuming that this body in liquid form was much denser than soluble sulphur, his theory was that its production caused a shrinkage which reduced the natural expansion of the sulphur. He made a series of measurements of the amounts of insoluble sulphur obtained by chilling sulphur which had been kept at various temperatures and found that the amount rose steadily to 22.6 per cent. at 179.4°. At 213.5° it was 27 per cent. and at higher temperatures about the same. Thus he thought that either the proportion of insoluble sulphur became constant above 180°, or possibly the whole of the sulphur had been transformed into this modification. In either case the coefficients beyond that temperature were those of a substance whose composition no longer changed.

Moitessier observed that a certain length of time was required before the sulphur reached a state of equilibrium at each temperature. Thus when a charged dilatometer was suddenly moved from a bath in which it had been kept at 140° to one of which the temperature was 171° the following were some of the readings which were obtained at intervals of a minute:

Time.	1′.	2′.	3′.	4′.	5′.	6′.	7′.	8′.	15′.
Reading.....	47.5	48.2	48.5	49.0	48.5	47.9	47.8	47.8	47.8

Apparently the sulphur reached the new temperature in four minutes and showed at that time its maximum volume. Three minutes more were needed, however, for the accomplishment of an internal change, and the constant volume was reached at the end of seven minutes from the start. It will be noted that in this experiment the material had to undergo the transition which we have found to occur at 160°. A similar experiment in which the dilatometer was brought rapidly from 135° to 163° showed a much smaller effect:

Time.	1′.	5′.	7′.	15′.
Reading.......	45.0	47.5	47.0	47.0

The Method Used for the Dilatometric Determination of the Transition Point.—When an experiment corresponding to the above is made with solid sulphur in the neighborhood of 95.6°, the dilatometer being filled up with oil, the new temperature is reached in a few minutes, but the change in volume continues for many hours. The transformation of rhombic into monoclinic sulphur, or *vice versa*, which then occurs is a very slow process. It was easy therefore for Reicher[1] to find two temperatures, one degree apart, at the lower of which monoclinic sulphur changed into rhombic with steady contraction while at the higher the opposite change went on with expansion. At a temperature midway between these points no change in volume was observed. In the present instance the transition in the melted sulphur is accomplished almost as soon as the new temperature is reached, and hence the volume-changes accompanying the two phenomena are superposed and difficult to distinguish. Reicher's method is thus inapplicable to the transition from S_λ to S_μ. We therefore decided to determine the location of the transition point more exactly by measuring the dilatations in the neighborhood of the point at shorter intervals than those used by Moitessier.

The form of the apparatus, and the method of maintaining a succession of constant temperatures were the same as those employed in the observations of the onset of viscosity. The bulbs of the dilatometers held about 20 cc. and a length of the attached capillary tube equal to one division on the arbitrary scale employed contained approximately 0.0004 cc. The dilatometer, after being filled, was kept at the first temperature for one to one and a half hours to permit complete adjustment of the sulphur to a condition of equilibrium. At each succeeding temperature the final reading was not recorded until a number of tentative observations had shown that the volume had become constant. In this way the sulphur remained from twenty-five to forty minutes at each temperature. Near to the transition point readings were made at intervals of 1°.

The materials used were: (1) sulphur twice distilled; (2) sulphur twice distilled, then melted and treated with ammonia; (3) recrystallized sulphur, melted and treated with ammonia. There were two sets of observations in each of these three cases. The first, with an ascending series of temperatures, involved the transition from S_λ to S_μ. The second, made immediately afterwards with the same filling of the dilatometer, involved the opposite transition with a descending series of temperatures.

The dilatometer used in the first and the last of the three sets was calibrated in order that the actual coefficients of expansion

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[1] *Zeit. für Krystallographie*, **8**, 593 (1884).

might be ascertained. For the mere purpose of locating the transition point, however, calibration and allowance for the coefficient of expansion of the glass were unnecessary. In the following table, therefore, the uncorrected readings have been used. In the columns headed "Mean temperature" the mean of the temperatures corresponding to two successive readings are given. In the other columns, headed "Expansion for 1°," is given the expansion per degree between two successive temperatures, expressed in terms of the divisions of the arbitrary scale. Thus in the first column 161.3° is the mean of the successive temperatures 160.8° and 161.9°. The expansion on the scale for this difference of 1.1° was 4.7 divisions, or 4.3 per degree.

Distilled S. Ascending series.		Distilled S + NH_3. Ascending series.		Crystallized S + NH_3. Ascending series.	
Mean Temp.	Expansion for 1°.	Mean Temp.	Expansion for 1°.	Mean Temp.	Expansion for 1°.
154.2	17.3	156.6	13.9	154.4	17.5
156.2	13.7	158.4	6.8	157.8	10.8
157.9	8.9	159.9	3.0	160.2	2.6
159.2	6.3	161.1	3.2	161.3	2.9
160.2	4.6	162.2	3.6	162.6	4.2
161.3	4.3	163.5	4.4	164.1	4.4
162.4	4.8	165.0	5.0	166.1	5.4
163.7	5.0			168.3	6.8
166.0	5.6				
168.9	7.0				
Descending series.		Descending series.		Descending series.	
169.9	7.8	167.3	5.8	168.9	7.1
167.7	6.3	165.3	5.4	166.9	6.5
164.6	5.3	162.8	3.6	164.7	6.1
162.4	4.3	160.1	2.8	163.0	4.9
160.8	4.3	157.6	9.8	161.4	4.3
159.8	4.5			160.3	5.0
157.9	9.0			158.7	7.7
154.9	16.9			156.9	13.3
				155.2	16.0

By graphic interpolation, using each of the six sets of observations separately, the following values for the transition point were found:

	Ascending.	Descending.
Distilled sulphur.................	160.2	160.2
Distilled sulphur + ammonia.....	160.0	160.2
Crystallized sulphur + ammonia..	160.2	160.0

The mean of all the results is 160°. It will be seen that there is no difference between the behavior of the samples which, by treatment with ammonia, had lost the capacity by chilling to give insoluble sulphur, and those which had not. In each case a part of the same specimen was chilled in order to make sure that the treatment had been effective.

The Actual Value of the Coefficients of Expansion of Sulphur near to the Transition Point.—The dilatometer used in the first two of the above three series of measurements had been calibrated, so that the actual values of the coefficients of expansion in this interesting region could be learned.

The capillary tube was fairly uniform in bore and no corrections were made for the very slight irregularities. The bulb and capillary were in all cases completely immersed in the bath, so that no correction was required on this account. The constants of the dilatometer were as follows:

	cc.
Volume of dilatometer at 0° up to zero of arbitrary scale	19.738
Volume of capillary per centimeter at 21°	0.00616
Volume of capillary per scale division at 21°	0.000414

100 scale divisions = 6.72 cm.

Coefficient of expansion of the glass ≐ 0.000029

By calculation, the volume of 1 scale division at 160°, allowing for the expansion of glass, is 0.000415 cc. By calculation, the volume of the bulb to the zero of the scale, allowing for the expansion of the glass, in cubic centimeters and in scale divisions, is: 150°, 19.824 cc. = 47768 scale divisions; 160°, 19.830 cc. = 47782 scale divisions; 170°, 19.836 cc. = 47796 scale divisions. Volumes at intermediate temperatures were obtained from above by interpolation.

In the following tables the second and third columns give the temperature and scale readings. The thermometer employed was compared with a standard thermometer at 100° and agreed with it within 0.1°. The fourth column gives the difference between successive scale readings divided by the difference between the corresponding successive temperatures; this is the apparent expansion per degree. The first column shows the mean of two successive temperatures and the fifth column the corresponding coefficient of expansion. The first series was made with distilled sulphur, and the second with melted crystallized sulphur which had been treated with ammonia. In each of the two series the first set of readings was made with rising and the second with descending temperature.

COEFFICIENT OF EXPANSION. FIRST SERIES. DISTILLED S.

Mean temp.	Temp. reading.	Scale reading.	Apparent expansion for 1°.	Coefficient.
	153.2°	0.0		
154.2°	155.2°	34.7	17.3	0.000363
156.2°	157.2°	62.2	13.7	0.000287
157.9°	158.7°	76.0	8.9	0.000192
159.2°	159.6°	81.4	6.3	0.000125
160.2°	160.8°	87.0	4.6	0.000097⊕
161.3°	161.9°	91.7	4.3	0.000089⊕
162.4°	163.0°	97.0	4.8	0.000102
163.7°	164.5°	104.5	5.0	0.000104
166.0°	167.5°	121.2	5.6	0.000116
168.9°	170.4°	141.5	7.0	0.000146
	170.5°	142.8		
169.9°	169.4°	134.2	7.8	0.000163
167.7°	166.0°	112.6	6.3	0.000132
164.6°	163.3°	98.2	5.3	0.000111
162.4°	161.5°	90.5	4.3	0.000089
160.8°	160.2°	84.9	4.3	0.000090⊕
159.8°	159.4°	81.3	4.5	0.000094
157.9°	156.4°	53.2	9.0	0.000195⊕
154.9°	153.5°	4.2	16.9	0.000338

COEFFICIENT OF EXPANSION. SECOND SERIES. CRYST. $S+NH_3$.

Mean temp.	Temp. reading.	Scale reading.	Apparent expansion for 1°.	Coefficient.
	152.8°	15.3		
154.4°	156.0°	71.4	17.5	0.000367
157.8°	159.7°	111.3	10.8	0.000225
160.2°	160.8°	114.2	2.6	0.000055⊕
161.3°	161.9°	117.4	2.9	0.000060⊕
162.6°	163.3°	123.3	4.2	0.000088
164.1°	165.0°	130.8	4.4	0.000092
166.1°	167.2°	142.7	5.4	0.000112
168.3°	169.4°	157.6	6.8	0.000141
	169.5°	130.5		
168.9°	168.4°	122.7	7.1	0.000048
166.9°	165.5°	103.7	6.5	0.000136
164.7°	164.0°	94.5	6.1	0.000128
163.0°	162.0°	84.7	4.9	0.000102
161.4°	160.8°	79.5	4.3	0.000090⊕
160.3°	159.8°	74.5	5.0	0.000104⊕
158.7°	157.7°	58.2	7.7	0.000162
156.9°	156.2°	38.2	13.3	0.000279
155.2°	154.3°	7.8	16.0	0.000335

In order to secure mean values for the coefficient, all the results were laid down graphically (temperature horizontally and coefficient vertically) in Fig. 2 and a smooth curve was drawn through them. The only points to be regarded as thoroughly trustworthy were those derived from temperature readings, both of which were certainly upon the same branch of the curve. When the readings are on opposite sides of the minimum the point based on them does not show the true direction of the curve. The points about which there can be no question are marked thus: +. The others, indicated by the sign ⊕ upon the diagram and in the tables, are based upon readings, one of which was within the region of uncertainty, 159.8-161°. A little consideration will show, however, that of these values the ones corresponding to the lowest coefficients must be the most accurate. In making the curve the two lowest points of this kind have therefore been given the most weight. The following table gives the values of the coefficients of each degree between 154° and 170°, as they may be read from the curve. The mean error outside of the region 1° on each side of the minimum, calculated by taking the average of the vertical distances of the points from the curve, excluding, however, the points marked, ⊕ is ±0.000007.

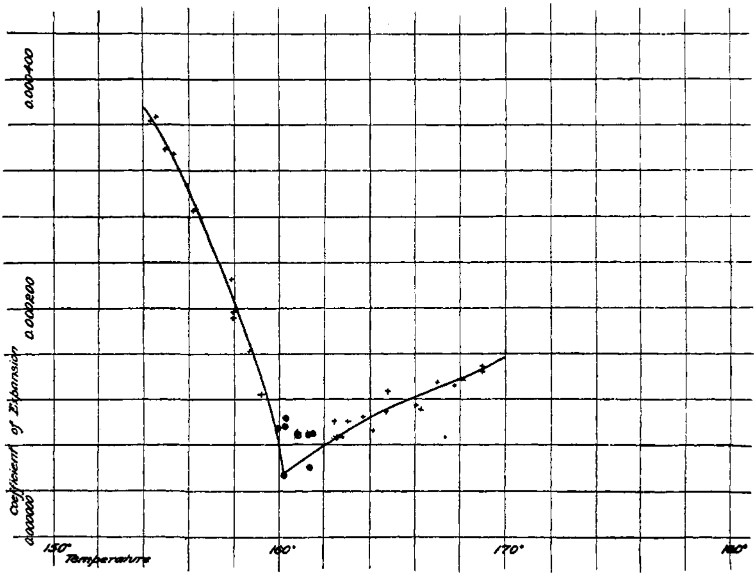

Fig. 2.

MEAN COEFFICIENTS OF EXPANSION.

Temp.	Coefficient.	Temp.	Coefficient.
154	0.000376	162	0.000084
155	0.000340	163	0.000096
156	0.000300	164	0.000106
157	0.000252	165	0.000114
158	0.000204	166	0.000124
159	0.000148	167	0.000130
160	0.000076	168	0.000140
160.2	0.000058(min.)	169	0.000148
161	0.000068	170	0.000158

The values for intervals of 20°, such as Moitessier gives, are shown by the above results to be very rough averages for regions in some parts of which the coefficient is six times as great as in others. Thus, for 140-160° he gives the value 0.000380 and for 160-180°, 0.000210. The change in the coefficient is much more extensive and sudden than his results would lead one to expect.

The Transition Point Elevated by a Dissolved Substance.—As has been said, one of our objects was to ascertain whether samples of sulphur, which on being chilled gave insoluble sulphur, showed the same transition point as those which did not. The identity in the values of the transition point found by use of each kind was to be used as a proof that no substance was present at the transition point in the former set of samples that was not present in the latter. To make this inference valid, however, it was necessary to show that a foreign substance purposely introduced did displace the transition point.

Preliminary experiments, made in connection with the observations of the onset of viscosity (Section 2) and of the heat absorption (Section 3), showed that there was such a displacement. Thus with 2 per cent. of phenol the first appearance of viscosity was noticed about 7° above the usual point. Exact measurements, however, could not be made by either of these methods. Further, evidence that there is an elevation in the transition point when phenol is dissolved in sulphur was obtained in connection with the measurement of the solubility of sulphur in phenol, and has been referred to in that connection.

Since the dilatometric method gave the most exact determinations of the transition point, two sets of experiments were made by that method. In these phenol, on account of its well-known tendency to association, was not employed. Two solutions of triphenylmethane in melted sulphur containing respectively 1 and 2 per cent. of the organic substance were used. The observations were carried out in the same way as those described above, and the data are expressed in the same fashion as before:

Dist'd S + 1 per cent. $CH(C_6H_5)_3$.
Ascending series.

Mean temp.	Expansion for 1°.
149.8	11.7
153.5	11.7
157.1	10.2
159.5	7.5
162.5	3.2
164.5	2.9
166.5	3.4
168.5	3.7
170.7	4.4
173.0	4.8
Descending series.	
172.4	5.0
169.4	4.1
166.7	3.4
(163.2	3.6)
159.4	7.4
157.0	10.2
Extra readings	
164.2	2.9
161.7	4.2

Dist'd S + 2 per cent. $CH(C_6H_5)_3$.
Ascending series.

Mean temp.	Expansion for 1°
159.2	11.4
161.4	9.8
164.0	6.1
166.5	4.5
167.5	5.0
169.4	5.0
172.2	5.3
175.4	5.7
Descending series.	
179.5	5.9
176.1	5.4
172.2	5.4

The numbers enclosed in parenthesis were derived from two successive readings at 165.5° and 160.9°. These temperatures were too far apart and lay on opposite sides of the new transition point. Since, therefore, they belonged respectively to the left and right arms of the curve, the numbers derived from them in the usual way did not represent the true direction of the curve at 163.2°. Two extra readings, avoiding these sources of error, were therefore made and were employed in constructing the curve.

The transition points, found by graphic interpolation, were as follows:

Sulphur + 1 per cent. triphenylmethane...............	163.0°
Sulphur + 2 per cent. triphenylmethane...............	165.6°

The value for sulphur alone being 160°, the elevations of 3° and 5.5° respectively are approximately proportional to the amounts of the dissolved substance. The molar elevations, for one mole of triphenylmethane in 100 grams of sulphur, calculated from these data are 700 and 660, the mean of the values being 680.

Dilatation at 220-266°.—As we have seen, Frankenheim expresses himself confidently in regard to a point lying between 250° and 260° at which a marked absorption of heat takes place. In spite of the fact that other observers, including ourselves, had discovered no definite evidence of the existence of such a point, it seemed worth while to investigate this region by means of the dilatometer.

The observations were made with crystallized sulphur which had been melted and treated with ammonia. The same apparatus as before was employed. The inner tube, in which the dilatometer was placed, contained phthalic anhydride. The bath was charged first with diphenyl and, at the higher temperatures, with diphenylmethane. The temperature was varied as before by altering the pressure under which the substance in the outer tube boiled. The readings were made at intervals of 3-5°. The results were as follows:

Cryst. S + NH_3.		Cryst. S + NH_3.	
Mean temp.	Expansion for 1°.	Mean temp.	Expansion for 1°.
222.6	13.3	247.9	13.5
227.6	13.4	252.7	13.6
234.5	13.1	258.1	13.5
239.6	13.1	262.9	13.8
243.7	13.2		

There was thus no evidence of any change in the dilatation between 220° and 266°.

VI. DIRECT OBSERVATION OF THE SEPARATION INTO TWO PHASES.

When pure, redistilled sulphur is melted in a test-tube and heated until it becomes viscous the separation into two phases is easily observed as the liquid cools. In consequence of the relatively greater surface of the bottom of the tube and the more rapid loss of heat at this place, the lowest part of the sulphur is the first to pass into the pale yellow form. The interface between this portion and the dark brown material above is at first very distinct. It recedes gradually up the tube, but soon vanishes in consequence of the progress of the transformation within the upper layers themselves and the gradual increase in mobility and decrease in depth of color in this region. If the tube is kept in a bath at 158-160° the upward movement of the interface can be followed for a much longer time.

It was thought, at first, that a method of determining the temperature of the transition might be founded upon this, by varying the temperature of the bath until a point was discovered at which the interface remained constantly in the same position. But it was found that, even at temperatures very little below the transition point, the change went on within each mass, as well as at the interface, so that the sharpness of the plane of demarkation could not be maintained for a sufficient length of time.

RESULTS OF THIS INVESTIGATION.

(1) With melted rhombic sulphur the appearance of easily perceptible viscosity takes place first at 159.5°.

(2) The absorption of heat connected with the transition occurs at 162.5° and upwards, and the liquid becomes viscous at the same moment. The temperature falls to 162°, and the transition is therefore not higher than this temperature.

(3) Distilled sulphur does not show any sharp onset of viscosity or noteworthy absorption of heat and appears therefore to be more subject to superheating than is recrystallized sulphur.

(4) These phenomena take place in the same way and at precisely the same temperature whether the sulphur concerned is such as by chilling gives insoluble sulphur or, having been treated with ammonia, does not.

(5) The existence of two independent curves of solubility for the two kinds of liquid sulphur in triphenylmethane and other solvents is demonstrated. The solubility of yellow mobile sulphur (S_λ) increases; that of brown viscous sulphur (S_μ) decreases with rise in temperature.

(6) The expansion of yellow mobile sulphur (S_λ) diminishes rapidly from 154° to 160°; that of brown, viscous sulphur (S_μ) increases rapidly from 160° upwards. The statement under (4) holds in this case also.

(7) The coefficients of expansion of sulphur for short intervals of temperature from 154-170°, covering the regions on each side of the transition, are determined.

(8) The dilatometric method gives no evidence of the existence of Frankenheim's transition point (250-260°).

(9) It is shown that the point of minimum dilatation is displaced upwards when triphenylmethane is dissolved in the sulphur. The displacement averages 2.8° for 1 per cent. of this foreign body.

(10) An experiment is described in which the separation of the two phases, yellow and brown liquid sulphur, may be observed.

(11) It is thus shown conclusively that there are two liquid states of sulphur which are partially, but only partially, miscible. These are S_λ, which predominates from the melting-point to 160°, and S_μ, which prevails above 160°. As the temperature ascends, saturation of the former with the latter determines the separation of the new phase, and conversely when the temperature falls.

REACTIONS IN LIQUID AMMONIA.[1]

By Edward Curtis Franklin.

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INTRODUCTION.

The striking parallelism between the general properties of liquid ammonia and water has been emphasized by the writer and his co-workers in previous papers.[2] Water, among solvents, is characterized by its high boiling-point, its high specific heat, its high heat of volatilization and heat of fusion, its high critical temperature and pressure, its high association in the liquid condition, its high dielectric constant, by its low boiling-point elevation constant, by its power to unite with salts as water of crystallization, by its wide solvent power, and by the fact that, with the possible exception of hydrocyanic acid, it is the most powerful ionizing solvent known. Aqueous solutions of salts are also, generally excellent conductors of electricity.

Of all well-known solvents ammonia most closely approaches water in all those properties, which give to the latter its unique position among solvents. While the boiling-point of liquid ammonia is 33.6° below zero, it still appears abnormally high when compared with the boiling-points of such substances as methane, ethylene, hydrogen sulphide, phosphine, arsine, hydrochloric acid,

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[1] Presented in abstract at the Philadelphia Meeting of the American Chemical Society.

[2] Franklin and Kraus: *Am. Chem. J.*, **20**, 820 and 836 (1898); **21**, 8 (1899); **23**, 277 (1900); Franklin and Stafford: *Ibid.*, **28**, 83 (1902).