

absorption spectra of erbium from different sources are noticeable and while it is too early to give any detailed description of the changes observed it does seem well to call the attention of chemists, working on the rare earths, to this peculiarity in the hope that it may be confirmed and the separation made.

A considerable amount of gadolinite and xenotime is now being worked up and separated for purposes of future research.

In conclusion I wish to thank Professor Charles L. Parsons for advice and the interest he is taking in the work; and acknowledge my indebtedness to the Welsbach Light Company for raw material received through the courtesy of Dr. H. S. Miner.

NEW HAMPSHIRE COLLEGE.
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[CONTRIBUTION FROM THE LABORATORIES OF GENERAL AND PHYSICAL CHEMISTRY
OF THE UNIVERSITY OF CHICAGO.]

ON AMORPHOUS SULPHUR: STUDY OF THE TWO FORMS OF LIQUID SULPHUR AS DYNAMIC ISOMERS.¹

BY CHARLES MACDONALD CARSON.

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In their first paper on amorphous sulphur it was shown by Smith and Holmes² that the freezing point of liquid sulphur is depressed below 119.25° to various extents and that the depressions are quantitatively in the direct ratio of the proportions of amorphous sulphur obtained by chilling the specimens immediately after the temperature of freezing has been read. In their second paper³ it was shown that there are two forms of liquid sulphur, S_{λ} and S_{μ} , of which the former is pale yellow and mobile and the latter is brown and viscous. These forms are miscible and exist in equilibrium with one another in proportions depending upon the temperature. It was shown that these two forms have different curves of solubility in solvents like triphenylmethane and that melted sulphur shows a very marked minimum of dilatation at 160° . It was suggested that the thermal effect and sudden increase in viscosity which occur just above this temperature were probably due to the separation of a new phase consisting of a liquid, the viscosity of which is due to increased proportions of S_{μ} . The third⁴ paper by the same observers dealt with the influence of foreign substances on the results of super-

¹ Read in abstract by Prof. Smith before the American Chemical Society at Ithaca, June 30, 1906. A paper with this title and embodying the conclusions reached in this paper is published in collaboration with Prof. Alexander Smith in the *Zeitschrift für Physikalische Chemie*, 57, 685.

² *Zeit. Phys. Chem*, 42, 469 (1903).

³ Smith, Holmes and Hall, this Journal, 27, 797 (1905). *Zeit. phys. Chem.*, 52, 602 (1905).

⁴ This Journal 27, 979 (1905). *Zeit. Phys. Chem.*, 54, 257 (1906).

cooling melted sulphur. Its chief conclusion was that amorphous sulphur is supercooled S_μ .

The work mentioned in the last paragraph has been continued under the direction of Professor Alexander Smith, and the results will be given in this paper. The rates of transformation of $S_\lambda \rightleftharpoons S_\mu$ in the presence of different catalytic agents have been determined and will be discussed first (Section I). For though in themselves of minor interest, the results are essential to the understanding of the observations described in later sections. The effect of iodine in causing a displacement of the equilibrium will be considered in Section II, but only so far as is required for the purpose of contrasting the results with those obtained when mere catalytic agents are used, as the question is not intimately connected with the main problems of this paper. New freezing-point determinations have been made so as to permit a full discussion of freezing-point phenomena (Section III). The purpose of Sections IV to VIII is to explain the increasing viscosity of liquid sulphur in the neighborhood of 158° , and the heat absorption occurring at some temperature between 160° and 170° when the liquid is heated rapidly. In Section IV experiments on the thermal effects are described; in Section V the measurements which give the exact proportions of S_μ at temperatures between 155° and 165° , and therefore the exact form of the equilibrium curve in that region, and in Section VI the changes in the concentration of S_μ when liquid sulphur is heated rapidly and is therefore not in equilibrium. A discussion of the increase in viscosity will be found in Section VII, and of the heat absorption in Section VIII.

I. The Influence of Catalytic Agents on the Rate of Transformation of
 $S_\lambda \rightleftharpoons S_\mu$.

In their study of the conditions under which amorphous sulphur is formed, Smith and Holmes¹ found that the percentage of S_μ that survives on chilling liquid sulphur depends very largely on the presence of certain foreign substances. For example, sulphur which had been recrystallized from carbon bisulphide and had stood exposed to the air for some days, was heated near its boiling-point for one hour and then chilled. On analysis it proved to contain 34 per cent. of the insoluble modification. When ammonia was passed into the melt, however, the capacity to give amorphous sulphur disappeared.

In view of the striking influence which catalytic agents have thus been shown to have on the behavior of liquid sulphur, a closer study of their effects was deemed advisable. Accordingly, a set of experiments was devised to subject to quantitative investigation the speed of transformation $S_\lambda \rightleftharpoons S_\mu$ in ordinary liquid sulphur.

¹ Loc. cit.

(1). Nine large test tubes each containing about thirty grams of re-crystallized sulphur were placed simultaneously in a glycerol bath, the temperature of which was maintained constant ($\pm 0.25^\circ$) at 130° . After various periods of from 30 to 300 minutes, counted from the time of complete melting, tubes were taken from the bath and broken into ice as quickly as possible. The hardened masses so obtained were dried and then extracted with carbon bisulphide, in a Soxhlet apparatus, so that the proportions of S_μ were determined.

Time of Heating at 130°	Per Cent. S_μ	Time of Heating at 130°	Per Cent. S_μ
30 minutes	0.2%	150	3.9
45 "	0.7	180	4.0
60 "	1.2	240	4.2
90 "	2.8	300	4.4
120 "	3.3	at equilibrium	4.3

(2). In this set the conditions were the same as in the preceding, except that the temperature of the bath was 140° .

Time of Heating at 140°	Per Cent S_μ	Time of Heating at 140°	Per Cent S_μ
15 minutes	2.1%	75 minutes	5.2
30 "	3.7	90 "	5.5
45 "	4.4	120 "	5.5
60 "	4.8	at equilibrium	5.6

It will be observed that after thirty minutes at these temperatures the liquid contains from 2 to 4% less of S_μ than it does when equilibrium has finally been reached. This result is important, especially in connection with the results of later sections dealing with the changes of concentration when the liquid is heated rapidly (Section VI) and the thermal effects in the neighborhood of 170° (Section IV).

Rate of Transformation $S_\mu \rightleftharpoons S_\lambda$ in Ordinary Liquid Sulphur.—The next set of experiments was intended to investigate the reverse of the preceding, that is the rate of change of $S_\mu \rightleftharpoons S_\lambda$.

(1) Three large test tubes each containing about 30 grams of ordinary sulphur were placed in a bath at 156.5° , a temperature chosen so as to be slightly below that at which the liquid becomes brown and viscous, and were left there for seven minutes after the sulphur had melted. One tube was then taken from the bath and broken into ice immediately, a second was held in the air for one minute while the contents were stirred with a thermometer, and the temperature was noted at the instant before the sulphur was chilled in ice, the third was treated like the second except that it was held in the air and stirred for two minutes.

Temp. of Bath	Time of Cooling in Air	Temp. before Chilling	Per Cent S_μ
156.5	0 minutes	156.5	7.9
156.5	1 "	135.0	7.3
156.5	2 "	121.5	7.1

(2). This set was similar to the preceding except that the temper-

ature of the bath was 160° , a temperature chosen so that it was slightly above that at which the sulphur becomes brown and viscous.

Temp. of Bath	Time of Cooling in Air	Temp. before Chilling	Per Cent. S_{μ}
160	1 minute	139	6.8
160	2 "	122	5.7
160	3 "	112	5.4

The results of the last two sets of experiments show that when the concentration of S_{μ} is small, the transformation $S_{\mu} \rightleftharpoons S_{\lambda}$ in sulphur containing sulphur dioxide proceeds with a measurable velocity. This will be again referred to in the section dealing with the determination of freezing points. (Section III).

The State of Equilibrium in the Presence of Ammonia.—Since liquid sulphur through which ammonia has been passed is incapable of giving any insoluble sulphur on chilling, it is important to learn what effect, if any, the ammonia has on the equilibrium between S_{λ} and S_{μ} . As the liquid still becomes brown and viscous above 160° , shows the same rate of expansion with changes in temperature, and the same solubility curve, it was considered likely by Smith and Holmes that the concentration of S_{μ} at equilibrium is the same as in the case of ordinary sulphur. In order to gain some decisive information on that point the following experiments were performed.

(1). Forty grams of sulphur were heated at 140° for one hour and a half, ammonia being bubbled through it at intervals. Powdered phosphoric acid was added at the end of that time and the whole was stirred for 10 minutes, after which the sulphur was removed from the bath and chilled. It was allowed to harden and was then analyzed. It was found to contain 5.8 % S_{μ} .

(2). This experiment was similar to the preceding except that sulphuric acid was substituted for phosphoric. In this case, 5.8 % of S_{μ} was obtained. Separate experiments showed that both phosphoric and sulphuric acids act as retarding agents to the same extent as sulphur dioxide so that the concentration of S_{μ} could not change greatly after their addition.

Since at equilibrium the concentration at 140° is 5.6 % of S_{μ} , it is evident that that state had been reached in the presence of ammonia, the acids serving merely to prevent the reversion of S_{μ} to S_{λ} when the melt was chilled. Further evidence confirming this conclusion will be found in the next paragraph.

Effect of Ammonia on the Rate of Transformation $S_{\mu} \rightleftharpoons S_{\lambda}$.—

(1). Four large test tubes each containing about 40 grams of ordinary sulphur were placed in a bath whose temperature was initially 122° . When all the solid had melted, dry ammonia was passed into the first lot for three minutes, sulphur dioxide into the other three for the same length

of time. The bath was then heated at the rate of two degrees per minute till 155° was reached when the temperature was held constant.

Sulphur dioxide was at once passed into the first tube for three minutes in order to displace the ammonia and immediately the first and second tubes were withdrawn from the bath and plunged into ice. The third and fourth were left at 155° for one and two hours respectively, after which they were treated like the first two. Analyses were made two days later.

Number of Tube.....	1	2	3	4
Per Cent. S_{μ}	7.4	5.7	6.8	7.2

We may conclude that in the presence of ammonia the liquid has reached in 15 minutes the same state that it would reach in two hours in the presence of sulphur dioxide.

(2). Three samples of sulphur were melted with the least possible superheating, viz. at 121° . The first was treated with ammonia for three minutes, then immediately with sulphur dioxide for three minutes, the other two were treated with sulphur dioxide alone for six minutes. The first and second were chilled at once, the third after one hour.

Number of Tube.....	1	2	3
Per Cent. S_{μ}	3.8	0.08	2.2

These results illustrate the rapid rate of transformation under the influence of ammonia, the slow rate under the influence of sulphur dioxide, and also the small amount of S_{μ} present in the liquid just after fusion.

(3). Ammonia was bubbled through sulphur which had been fused at 125° . The sulphur was heated at the rate of two degrees per minute, till it became viscous and showed a fall in temperature at 161.5° . Another sample which had been treated with sulphur dioxide became viscous at 167° , while a third, through which ammonia had been bubbled at 125° , was heated to 155° , sulphur dioxide was then passed through it while the temperature was still rising till it became viscous suddenly at 163° .

This experiment again illustrates the fact that the liquid eventually reaches the same condition whether under the influence of ammonia or of sulphur dioxide, the difference being one of rate of change.

It will be seen from the last three sets of experiments that in the estimation of the percentages of S_{μ} in liquid sulphur through which ammonia has been passed, it is necessary to add a retarding agent before chilling the melt, otherwise all of the S_{μ} will revert to S_{λ} . It was not possible by that method to determine how long the liquid required to attain equilibrium. Not only did the equilibrium change somewhat during the addition of the retarding agent, but the method of analysis is accurate only to within 0.2 or 0.3%. It would be advantageous to know, exactly, the length of time required to reach equilibrium when ammonia is the catalytic agent, or to know what percentages of S_{μ} the liquid con-

tains when heated rapidly to 160°. The importance of such knowledge will be apparent after the sections on the heat absorption between 160° and 170° have been read (Sections IV and VIII).

The method of passing ammonia into the liquid in order quickly to produce equilibrium, followed by the use of sulphur dioxide in order to preserve the relations on chilling, has been of service in estimating the proportions of S_μ in the liquid when at equilibrium at various temperatures. An experiment may be performed in that way in 30 minutes, whereas two hours are required for simply heating ordinary sulphur till equilibrium is reached.

II. *The Influence of Iodine on the State of Equilibrium.*

The addition of a foreign substance to liquid sulphur may cause two different effects. It may produce a permanent displacement of the state of equilibrium for each temperature, or it may influence only the rate of transformation $S_\lambda \rightleftharpoons S_\mu$. The second effect has been fully discussed in Section I and will be emphasized throughout this paper, especially in contrasting the influences of sulphur dioxide and of ammonia.

The addition of small amounts of iodine to molten sulphur was observed by Smith and Holmes¹ to produce a permanent displacement of the equilibrium conditions. The equilibrium curve for two parts of iodine to one hundred parts of sulphur and also the displacements of the equilibrium by different amounts of iodine at 150° have been given by Smith and Holmes.

Other results which will permit a comparison with the equilibrium in ordinary sulphur are given here in tabular form.

Temperature	Parts iodine to one hundred of sulphur	Percentages of S_μ			
		0	0.5	1	2
150°		6.7	11.2	12.4	13.8
140°		5.6	8.1	9.2	—
135°		—	—	—	8.6
130°		4.2	6.6	7.4	—
120°		3.8	4.9	5.2	5.3

The freezing points with corresponding concentrations of S_μ are as follows:

Parts Iodine	Freezing Point	Per Cent S_μ
0	114.5	3.7
0.5	113.9	4.3
1	113.4	4.7
2	112.5	not determined

Since analysis shows the same results whether the superheating has been for only ten minutes or for three hours, it may be inferred that when iodine is present in the liquid equilibrium is reached in a few minutes. A few experiments were made in order to determine the rate of recession $S_\mu \rightleftharpoons S_\lambda$ in presence of iodine, of which the following is an

¹ This Journal 27, 997 (1905).

example. Three portions each consisting of 32 grams of recrystallized sulphur were heated in test tubes at 156° and ammonia was passed through them. Iodine was then added to each in the proportion of two parts to 100 parts of sulphur and the temperature was kept constant for 25 minutes. The tubes were then broken into ice after being held in the air for 0, 1 and 2 minutes respectively.

Time of Cooling in air	Temperature before Chilling	Per Cent S_{μ}
0 minutes	156	18.0
1 "	135	9.51
2 "	126	4.74

The recession of S_{μ} is seen to be much more rapid than that previously observed with sulphur containing sulphur dioxide (Section I) where the percentage fell in the same time from 7.9 only to 7.1. The result shows that iodine is a less efficient retarding agent than is sulphur dioxide, and so far as its catalytic effect on the fused mass is concerned, should yield smaller instead of larger proportions of amorphous sulphur.

With one tenth part of iodine, the sulphur is only slightly viscous even at 180° . With somewhat larger proportions of iodine the liquid is quite mobile at all temperatures.

III. The Depression of the Freezing Point of S_{λ} ; the Natural Freezing Point; and the Lowest Freezing that Has Been Determined.

It was first clearly pointed out by Gernez¹ that sulphur always freezes at some temperature below its melting point. His experimental work has been fully discussed by Duhem² who has given an explanation of the facts based on his own very thorough thermodynamical treatment of so-called "permanent changes." In three papers on "The Equilibria of Stereoisomers" Bancroft³ has rendered Duhem's work more accessible by substituting the graphical treatment for the analytical and applying this to the consideration of many organic substances which resemble sulphur in freezing at temperatures below their melting points. Any substance that exhibits that phenomenon is capable of existing in two solid forms which usually melt at different temperatures, but always give liquid systems of identical constitution in which the liquid states of the two forms co-exist in equilibrium. The name dynamic isomerides⁴ is now generally used to designate the two forms of such substances and will be applied in this paper to the two forms of sulphur, of which one, S_{λ} , may be obtained in the solid condition either as monoclinic or rhombic crystals according as the temperature is above or below 96° , and is soluble in

¹ Jour. de Phys. (1) 5, 212 (1876).

² Zeit. physik. Chem. 22, 545; 23, 193, 497 (1897).

³ Jour. physik. Chem. 2, 148, 245 (1898) 3, 144 (1899).

⁴ See Findlay, *The Phase Rule*, for numerous references to papers on dynamic isomerism.

carbon bisulphide, while the other, S_{μ} , may be isolated only in the well known amorphous, insoluble condition.

In the first paper, Smith and Holmes described freezing point observations in₃ which for the first time concomitant measurements of the proportions of insoluble sulphur were secured. The freezing points ranged from 118.3° with 0.7 percent of insoluble sulphur to 112.45° with 5.3 percent. By extrapolation 119.25° was found as the freezing point corresponding to 0 per cent of insoluble sulphur and the depressions below this temperature were shown to be strictly proportional to the amounts of insoluble sulphur present.

New Observations of the Freezing Point.—In the observations just mentioned, the sulphur contained the natural proportion of the retarding substance, namely, sulphur dioxide. The material was heated rapidly to a distance above the melting point, fitted to give approximately the content of S_{μ} required. On being removed from the bath or flame it cooled quickly to a temperature near to the freezing point and the determination was at once carried out in a Beckmann apparatus.

The following typical freezing points are chosen from about forty new observations in which the treatment before freezing was varied from that just mentioned in the ways described in the column headed "remarks." Several of these five were repeated a number of times without any change in the result.

No. of Exp.	Freezing Point	Parts S_{μ} with 100 S_{λ}	Remarks
1.....	114.5°	0.0	NH_3 at 448° for 15 mins.
2.....	114.4°	0.0	NH_3 , S boiling for 10 mins.
3.....	114.5°	1.5	CO_2 at 448° for 3 hours.
4.....	113.74°	0.9	Distilled S at 160° for 3 hours.
5.....	119.1°	trace	Melted at 125° and cooled quickly.

In a number of experiments of which Nos. 1 and 2 are samples, it seemed that sulphur which gave no S_{μ} on chilling should freeze close to 119.25° . In view of the study of the influence of catalytic agents (Section I), however, it is evident that in the presence of ammonia, which had been led through the sulphur before freezing, there was present the normal amount of S_{μ} corresponding to the temperature (3.7% at 114.5°) and therefore freezing above that temperature was impossible. The apparent absence of S_{μ} is due to its rapid reversion to S_{λ} during the subsequent chilling.

Gernez's observation of 114.4° as the final freezing point of liquid sulphur may be readily understood. The prolonged heating to which he subjected the sulphur drove out most of the sulphur dioxide and the rate of recession of the S_{μ} became therefore extremely rapid, and this led to the same final result as is more readily observed in presence of ammonia.

Experiment No. 3 in which carbon dioxide was used to hasten the

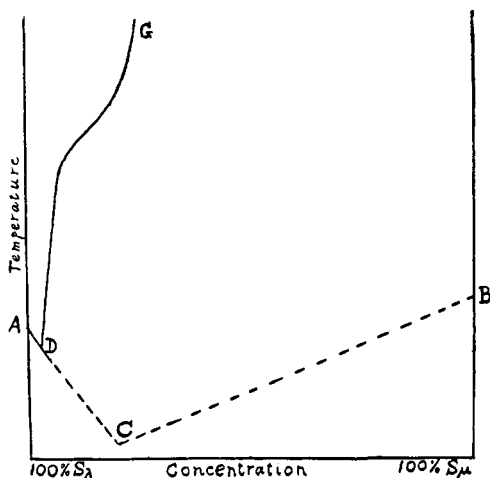
removal of the catalyser shows the effect of this treatment. Here the depression of the freezing point was that due to about 3.7 % of S_μ but only 1.5 % could be preserved by chilling.

In experiment No. 4 the retarding catalyser was partially removed by heating for three hours at 160° . Although the freezing point 113.74° is determined by about 4.2 % of S_μ only 0.9 % survived the chilling.

Experiment 5 illustrates the case where the full amount of the retarding agent is present and the melting, cooling and freezing operations are carried out at so low a temperature and so quickly that the S_μ scarcely has any opportunity to be formed.

Graphic Representations of the Final Conclusions.—The behavior of dynamic isomers has been represented in convenient graphic form by Bancroft¹. In a similar way, (Fig. 1), we may represent the results

FIG. 1.



already given by Smith and Holmes, together with those given in this paper (Section VI). The facts in regard to sulphur up to about 180° are shown to scale. Concentrations of S_λ and S_μ are plotted horizontally and the temperatures vertically. *A* is the freezing point of pure S_λ (119.25°). The descending continuous line, which extends to below *D* shows the freezing points with increasing proportions of S_μ . *B* is the freezing point of pure S_μ and is unknown. *BC* would show the freezing points of S_μ depressed by admixtures of S_λ . No such freezing points have been observed, however. *C* is the eutectic point and its location is also unknown. The line *AC* has been traced down to 112.45° (with 5.3 % of S_μ). This is the lowest freezing temperature for which it has been found possible to measure the corresponding concentrations of S_μ .

¹ Loc. cit.

by chilling. Whether the difficulty in getting observations below 112.45° is simply due to the lack of a more perfect retarding catalyser and may therefore be overcome by future work, or is due to the fact that 112.45° is itself the eutectic point and therefore the lowest possible freezing-point cannot at present be stated. DG is the curve showing the proportions of S_λ and S_μ in the liquid phase, at various temperatures. D is the final point of freezing, 114.5° , when, in presence of ammonia the system is in equilibrium with 3.7% of S_μ at the time of freezing. Such a point is called by Bancroft the "natural freezing point." It is a triple point at which liquid S_λ and S_μ , solid monoclinic sulphur, and sulphur vapor are in equilibrium. The curve DG runs from 114.5° , to 448° , the boiling point, but only that part from 114.5° to about 180° is shown. The corresponding concentrations of S_μ run from 3.7% (at D) to 34.1% at the boiling point.

IV. The Thermal Effects when Liquid Sulphur is Rapidly Heated or Cooled.

In a paper which appeared over a year ago, Smith, Holmes and Hall¹ described some careful experiments which seemed to indicate strongly the presence of a transition point in liquid sulphur in the neighborhood of 160° . Since this would be the first known example of a transition point in a liquid, further study of the question was considered advisable, and accordingly some new experimental data have been collected under the direction of Dr. Smith.

Schaum² had observed that when liquid sulphur is heated quickly, it usually suffers a slight fall in temperature at about 168° . The phenomenon was more fully investigated by Smith, Holmes and Hall, who noted that the fall in temperature is simultaneous with the well known increase in viscosity. They believed at that time that the important point was to determine the temperature at which the viscosity first begins to increase, when the liquid is heated so slowly that it is at all times very nearly in a condition of equilibrium. It appears at the present time, to be more advantageous to consider more fully the changes of temperature and of viscosity when the liquid is heated rapidly, especially as a new interpretation will be proposed for the results already published.

Influence of Catalytic Agents on the Temperature at which the Absorption of Heat Occurs.—Several series of experiments in an earlier part of this paper (Section I) have proved that, in the presence of certain catalytic agents, for example sulphur dioxide, the rate of transformation $S_\lambda \rightleftharpoons S_\mu$ is measurably slow, while in the presence of certain agents, such as ammonia, the rate is almost instantaneous. Many experiments have been made in order to learn what effect these agents have on the

¹ Loc. cit.

² Ann., 308, 25 (1899).

temperature at which the absorption of heat in rapidly heated liquid sulphur, occurs.

Experiments which show the effect of various catalytic agents; rate of heating, two degrees per minute.—The method of observing the thermal effects and at the same time any sudden changes in viscosity, was that which most readily suggests itself. A large glycerol bath was used and this was heated by a constant flame, so that the rise of temperature was nearly uniform.

Exp. 1. Forty grams of ordinary recrystallized sulphur were placed in a large test tube which was set in the glycerol bath, initially at 125° . When the solid had melted, a light glass stirring rod, and a thermometer graduated in half-degrees were inserted. The bath was then heated at the rate of two degrees per minute. At 167° , the thermometer indicated a sudden fall in temperature, and at the same instant the liquid became so thick that it could be stirred only with difficulty. The temperature was raised to 180° , and was then allowed to fall at the rate of one degree per minute. The liquid, which was still constantly stirred, became gradually more mobile, and at 157° was quite thin.

Exp. 2. This experiment was similar to the preceding, except that immediately after the sulphur was fused, sulphur dioxide was passed through it for two minutes. The fall in temperature with simultaneous thickening was noticed at 167° . When the liquid was cooled, it became mobile gradually. The experiment was continued by lowering the temperature to 130° , and again raising it at the usual rate. With rising temperature there was a gradual increase in viscosity above 159° , without any indication of a fall in temperature.

Exp. 3. The preceding experiment was repeated, except that after the sudden thickening at 167° had been noted, the bath was cooled to 116° . When again heated, at the usual rate, the liquid increased in viscosity gradually above 159° , but showed no fall in temperature. The liquid was then supercooled to 108° and again heated. The same gradual change above 160° was observed.

Exp. 4. This experiment was similar to the preceding, except that, after the sulphur had thickened at 167° , it was cooled to 112° , and allowed to solidify slowly. It was again fused and heated rapidly. It became viscous rather suddenly at 163° , and showed at the same time a slight fall in temperature.

It has been shown by Smith and Holmes that when the liquid is in equilibrium at 160° , it is brown and viscous, and contains 10.7% S_{μ} . When ordinary sulphur is heated rapidly as in the experiments described above, it does not reach that concentration until the temperature is several degrees higher than 160° . Consequently it becomes brown and viscous, not at 160° , but at some higher temperature, for example at 167° in the

experiment above. In the second parts of experiments 3 and 4 in which the liquid was heated a second time, the concentration of S_μ was from 3 to 4% higher at 125° than in experiment 1, so that the concentration sufficient to cause the increasing viscosity was reached at a much lower temperature, usually at about 160° instead of at 167° . When the liquid was allowed to solidify, part of the S_μ changed to S_λ so that on again fusing at 125° , the concentration was between that of freshly melted ordinary sulphur and that of sulphur which had been cooled from higher temperatures. The temperature at which the viscosity began to increase was consequently between 160° and 167° ; in the experiment described it was 163° .

Exp. 5. A specimen of sulphur was melted at 125° , and sulphur dioxide was passed through it for one minute. It was heated rapidly to 155° , then in 10 minutes from 155° to 158° afterward at the rate of two degrees per minute. The liquid became viscous gradually.

In this experiment the sulphur was given time to approach the condition of equilibrium somewhat more closely than when heated rapidly all the time, so that the concentration sufficient to cause the thickening was reached at a lower temperature.

Exp. 6. In an experiment in which the melt was treated with ammonia at 125° and then heated at the rate of two degrees per minute, the liquid became suddenly viscous at 161.5° , and suffered a fall in temperature at the same instant. After the liquid had been cooled from 180° to 155° , it was again heated rapidly, and again experienced the sudden change at 161° . It was then cooled to 158° and once more heated quickly. In this case the sulphur became viscous gradually. The results of this experiment were the same, when calcium oxide, hydrogen sulphide or potassium hydroxide was substituted for ammonia.

It is observed that, with catalytic agents which, like ammonia, accelerate the rate of transformation $S_\lambda \rightleftharpoons S_\mu$, the sudden increase in viscosity occurs always at about 161° when the liquid is heated rapidly. This may be observed repeatedly by cooling the liquid below 155° and again heating. Such a repetition is possible when ammonia is used, since when cooled the liquid adjusts itself nearly to a condition of equilibrium, and so is in the same state as when first treated with ammonia at 125° .

Exp. 7. One experiment will illustrate the behavior of sulphur which has been purified by distillation. A sample was fused at 125° and then heated at the rate of two degrees per minute. It increased in viscosity gradually from 160° onward.

Distilled sulphur thus behaved as if it contained a considerable amount of S_μ immediately after fusion.

Exp. 8. A sample which had been recrystallized from toluene showed the sudden thickening at 161.5° with accompanying fall of temperature,

and another which had been recrystallized from chloroform became viscous at 167° .

Exp. 9. Ordinary sulphur was fused at 125° and hydrogen chloride was bubbled through it for one minute. When it was heated at the rate of two degrees per minute, a sudden increase in viscosity, and slight fall in temperature were observed at 162.5° .

This temperature is slightly higher than when ammonia is used, so that hydrogen chloride evidently retards the rate of transformation to some extent.

*Similar Experiments by Hoffmann and Rothe.*¹—Quite recently some work on the absorption of heat by liquid sulphur has been carried out by Hoffmann and Rothe. They compared the rate of increase of temperature of the sulphur with that of a blank tube full of asbestos and air by means of a thermal element, and plotted the results in a diagram with times as abscissae and temperatures as ordinates. Since the rate of heating in their experiments was the same as in the experiments above, their results may be compared with those just given. They observed the heat absorption at 161.7° . Now we know from experiments already described that the temperature of heat absorption is as low as 161.7° only when some accelerating agent has been used or when the sulphur has been freshly recrystallized. It seems then that they must have used freshly recrystallized sulphur, though they do not mention the method of preparing the sulphur for their experiments.

Hoffmann and Rothe also found that, when the liquid was cooled at the rate of two degrees per minute, the temperature fell uniformly to 159.5° then quickly at the rate of 11, 8 and 4 degrees per minute for successive quarter minutes, afterwards uniformly at the rate of two degrees per minute. Smith, Holmes and Hall² over a year ago described a precisely similar experiment in which the heat absorption with rising temperature took place at 167.5° , while during cooling there was a rapid fall from 159.5° to 145° . They ascribed the latter phenomenon to "the adhesion of a mass of viscous, poorly conducting sulphur to the bulb of the thermometer and its sudden displacement by the mobile and cooler sulphur, from the layer, which, being nearer to the sides of the tube had lost heat more rapidly by radiation." Smith, Holmes and Hall emphasized the necessity of stirring in order to avoid this misleading phenomenon. Hoffmann and Rothe state explicitly, however, that they were not able to stir the viscous liquid without disturbing the temperature changes. Since the rapid fall in temperature is due to unequal heating, the experiment seems to be of no value in considering the cause of the heat effects in the neighborhood of 160° . In my own experiments in which

¹ Z. physik. Chem. 55, 113 (1906).

² Loc. cit.

the sulphur was constantly stirred, no irregularity in the rate of cooling was observed.

The influence of catalytic agents was also not appreciated by Hoffmann and Rothe. Thus they state that a little sulphuric acid, added so that the sulphur might be more easily stirred, since it has no chemical action on the sulphur, could not influence the thermal phenomenon. We have proved in this section, however, that the temperature of heat absorption is considerably raised by the presence of retarding agents such as sulphuric acid.

Variation of Temperature of Heat Absorption with Rate of Heating.—

It will be found later in this paper that in order to decide on the presence or absence of a transition point at 160° , it is necessary to have a full knowledge of the conditions under which the absorption of heat occurs when the sulphur is heated rapidly. Accordingly several experiments will be described here, in which the rate of heating was varied.

Exp. 10. The sulphur was melted at 125.5° and was immediately heated. The temperature of the melt was read at minute intervals. At 170.5° the temperature fell and the sulphur became viscous. The rate of heating was 2.5° per minute. The temperature was then allowed to fall. No irregularity in the rate of cooling was observed.

Exp. 11. Recrystallized sulphur was melted at 135.5° and immediately heated at the rate of 4° per minute. The fall in temperature and increase in viscosity were noted at 177.5° . The high value is accounted for, partly by the rapid rate of heating and partly by the high temperature at which the sulphur was fused. After heating to 190° the sulphur was allowed to cool at the rate of two degrees per minute. No irregularity in the rate of cooling was observed.

Exp. 12. It was found in the preceding set of experiments that sulphur which has been purified by distillation, becomes viscous gradually when heated rapidly. This experiment was accordingly conducted with distilled sulphur which was fused at 124° and then heated at the rate of 4° per minute. There was a slight absorption of heat at 162.5° , but the increase in viscosity was gradual.

By comparison of experiments 10 and 11, it will be seen that the more quickly the sulphur is heated, the higher is the temperature at which it becomes viscous. This may be readily understood, for the more rapidly the liquid is heated, the lower is the concentration of S_{μ} at each temperature and consequently the higher is the temperature at which the fixed concentration is reached, required for the production of the increasing viscosity.

Experiment 12 is confirmatory of experiment 5. Distilled sulphur when first melted contains more S_{μ} than does ordinary recrystallized sulphur. Accordingly, it will reach the concentration required for in-

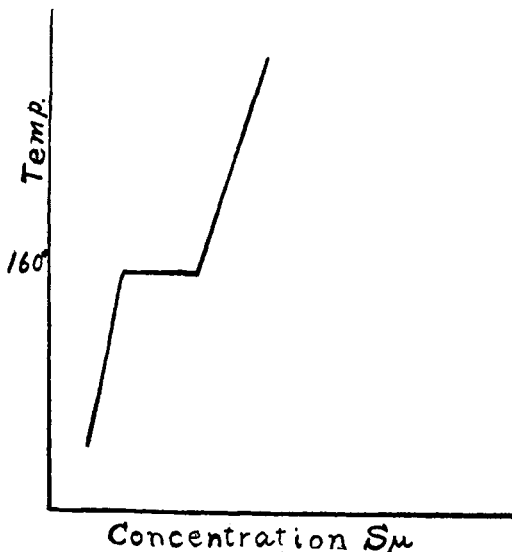
creasing viscosity at a lower temperature, usually at about 160° rather than at 167° , when the rate of heating is two degrees per minute. The lower the temperature at which the change in viscosity occurs, the more gradually does it appear. In all these experiments the liquid was constantly stirred, and the rate of cooling was nearly uniform. The sudden fall in temperature which was described by Hoffmann and Rothe, being due to mechanical effects, was not observed.

The results given in this section are in themselves an illustration of the effect of catalytic agents on the rate of transformation $S_\lambda \rightleftharpoons S_\mu$ (c.f. Section I). They will also be of use in deciding whether or not there is a transition point at 160° (See Section VIII). It will be advantageous, however, to postpone further discussion of their bearing on that question, till the actual changes in concentration when the liquid is heated rapidly have been considered.

V. Actual Form of Equilibrium Curve between 155° and 165° ; and Question of Possible Transition Point.

The fall in temperature and sudden thickening, which are usually observed at about 167° when liquid sulphur is rapidly heated, have been discussed at some length in this paper (Section IV). As has already

Fig. 2.



been mentioned, Smith, Holmes and Hall considered that the presence of a transition point at 160° would fully account for the phenomenon. They described some careful experiments which gave support to their

view, that at 160° two liquid phases may coexist, and that these differ only in the relative proportions of S_λ and S_μ which each contains.

The presence of two liquid phases of different concentrations at the same temperature would be indicated by a portion of the equilibrium curve being parallel to the concentration axis as represented in Fig. 2. Thus A and B would represent the percentages of S_μ in the phases of smaller and larger concentration respectively. The equilibrium curve, which has been given by Smith and Holmes, was plotted from results obtained some time before any work on possible transition points was begun, so that the part of the curve now under discussion was not considered of more importance than any other. Since the concentrations of S_μ had been determined at intervals of ten degrees, no information could be derived from the curve, relative to changes of concentration at constant temperature.

With the object of learning the exact course of the equilibrium curve close to 160° , the percentages of S_μ present at equilibrium, have now been determined for short intervals between 155° and 165° . In each experiment about forty grams of recrystallized sulphur contained in a large test tube were melted and dry ammonia was passed through the melt for five minutes. The tube was heated at first in a large glycerol bath and was then transferred to a smaller glycerol bath which was kept at constant temperature ($\pm .1$ degree) by the vapors of α -dichlorhydrin boiling under reduced pressure in an apparatus formerly used by Smith, Holmes and Hall¹. After the sulphur had remained at the desired temperature for fifteen minutes, a very slow stream of sulphur dioxide was passed through it for thirty minutes. The tube was then quickly removed and broken into ice. The analyses were made in the usual way.

Temperature	Per Cent S_μ	Temperature	Per Cent S_μ η
155.0	7.7	160.5	11.8
156.5	8.0	161.0	12.5
157.0	8.2	162.0	13.1
158.5	9.3	163.0	13.9
159.25	10.4	165.0	15.5
160.0	11.5		

These relations between S_λ and S_μ have already been represented in Fig. I. It will be noticed that no portion of the equilibrium curve between 155° and 165° is parallel to the concentration axis, so that between those temperatures, two phases of different concentration evidently do not exist in equilibrium with one another.

VI. Change of Concentration of S_μ when Liquid Sulphur is Heated Rapidly.

In section II, in which the effects of catalytic agents were discussed, it was pointed out that, when ordinary sulphur has been liquefied and

¹ Loc. cit.

then held for thirty minutes at 130° or 140° , the concentration of S_{μ} is still from 2 to 4% less than that required for equilibrium. Consequently when sulphur is melted at 125° and then heated at the rate of two degrees per minute, it will have at 160° much less of S_{μ} , than is possessed by the brown viscous liquid in equilibrium at that temperature. For that reason the liquid becomes brown and viscous only at some higher temperature, whose elevation above 160° depends on the kind of catalytic agent used, and on the rate of heating.

The actual change of concentration of S_{μ} , when the liquid is heated rapidly have been determined by separate experiments.

Exp. 1. Several lots of ordinary recrystallized sulphur, each contained in a large test tube placed in a glycerol bath, were fused at 121° . Sulphur dioxide was passed into each for two minutes and immediately one tube was removed from the bath and broken into ice. The bath was then heated at the rate of two degrees per minute, and at the desired temperature, tubes were removed and their contents chilled.

Temp. before Chilling.....	121°	154°	156°	160°	162°	165°	167°
% S_{μ} 2° per min.....	0.04°	5.4	5.7	—	6.4	7.5	10.3
% S_{μ} at equilibrium	3.75	7.5	8.0	10.7	13.5	15.5	16.7

The sulphur in the last tube had just begun to increase in viscosity.

Exp. 2. In this experiment the different specimens were heated rapidly to 167° , though each on a separate occasion. The attempt was made to chill them, while the temperature of the bath was still rising, at different stages during the rapid thickening, in order to discover what change of concentration takes place at that time. None was chilled later than one minute after the thickening had begun, so that, owing to the heat absorption, the temperature of the sulphur was below rather than above that at which the change had commenced.

Temp. of Chilling.....	167°	167°	167°	167°	167°
Per Cent S_{μ}	10.5	11.6	12.9	14.0	15.1

From these two experiments we may draw the following conclusions. When the liquid is first melted, the concentration of S_{μ} is extremely small. As the temperature is raised, the concentration of S_{μ} increases gradually, but at each temperature below 167° , is about 4% less than is required for equilibrium. At 167° the concentration necessary to produce the increasing viscosity is reached, and there follows a very rapid formation of S_{μ} . It is only when the temperature, at which the increasing viscosity begins, is somewhat above 160° that such a rapid formation of S_{μ} takes place, and consequently only then is there such a marked absorption of heat.

VII. *Dependence of the Increase in Viscosity on the Rate of Change of S_{μ} with the Temperature.*

The equilibrium curve of liquid sulphur is almost a straight line from the natural freezing point to about 158° . It then changes direction, since

from 158° to 165° the change of concentration of S_{μ} per degree is about 1%, while below 158° the change is only 0.12% per degree. In their work on the viscosity of liquid sulphur Bruulies and Dussey¹ found that the viscosity begins to increase at about 157° . It seems to be established that the increase in viscosity and change of concentration of S_{μ} with temperature are intimately connected. Assumptions might be made concerning the nature of S_{μ} with the object of explaining the pronounced viscosity but no experiments have been attempted which would serve as a foundation for a theory.

VIII. Discussion on the Cause of Heat Absorption.

Smith, Holmes and Hall² considered the most probable cause of the heat absorption when the liquid is heated rapidly to be the existence of a transition point at 160° . Those observers were careful to state, however, that the results of their dilatometric measurements did not constitute a proof of the presence of a transition point. The existence of such a point was inferred from solubility and thermometric determinations, and the only possible temperature at which a transition could occur was fixed by the dilatometric determinations. Smith, Holmes and Hall advanced the suggestion that at 160° two liquid phases with different concentrations of S_{μ} may coexist, and that when the change from the phase of lower concentration to that of higher takes place quickly, there is sufficient absorption of heat in a few moments, to cause a fall in temperature.

It has been pointed out (Section V) that with two phases of different concentration at the same temperature, the liquid would vary in composition while the temperature remained constant. But the determinations of the equilibrium proportions in the neighborhood of 160° have proved that the composition of the liquid changes only with the temperature. Consequently the coexistence of two liquid phases of such different concentration that the change from one to the other would involve a considerable heat effect is improbable. This conclusion is further supported by the fact that, when the liquid is heated very slowly, so that it is always very close to a condition of equilibrium, the onset of viscosity is gradual, thus indicating not a sudden but a gradual increase in concentration. Moreover the viscosity continues to increase up to about 180° , so that the cause of the increased viscosity must continue to operate continuously up to 180° .

Instead of assuming that there are two liquid phases of different concentration, we might suppose that at 160° , either of the two modifications changes to a new form. We could have, then, two different liquid phases which would give when chilled equal amounts of insoluble sulphur. We would expect, however, in that case that the viscosity would increase from 160° onward, so that such a transition is improb-

¹ *Compt. rend.*, 11^e, 1045 (1851.)

² *Loc. cit.*

able. This view will not be discussed at length, as the explanation advanced in the next paragraph seems to dispose of it effectually.

The experimental evidence submitted in this paper, not only proves the absence of a transition point, but leads to the true explanation of the heat absorption. In a preceding section, (V), the actual changes of concentration which take place when liquid sulphur is heated rapidly, were given. Attention was directed to the very rapid formation of S_{μ} which is coincident with and accounts for the sudden thickening, and for the fall in temperature. The more rapidly the liquid is heated, the higher must it be heated before a concentration is reached sufficient to produce the increased viscosity. When the liquid is heated slowly, it never differs much from a condition of equilibrium, so that the rapid formation of S_{μ} is impossible, and consequently no fall of temperature takes place.

I owe my thanks to Professor Alexander Smith, for the privilege of working on this problem, for much advice while the work was in progress and for the use of some of his unpublished results.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 131.]

RESEARCHES ON QUINAZOLINES (EIGHTEENTH PAPER), ON 2, 3-DIALKYL-4-QUINAZOLONES AND THE PRODUCTS OBTAINED BY ALKYLATING 2-ALKYL-4-QUINAZOLONES (2-ALKYL-4-HYDROXY QUINAZOLONES)¹

BY MARSTON TAYLOR BOGERT AND HARVEY AMBROSE SEIL.

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The tautomerism of the amide group, $-\text{CO.NH}- \rightleftharpoons -\text{C}(\text{OH}) : \text{N}-$, has interested organic chemists for many years and has led to many valuable investigations. These investigations have had to do not only with straight-chain fatty amides, but also with those of cyclic structure, as in the α -hydroxy derivatives of pyrrole, pyridine, pyrimidine, and similar heterocycles. The tautomerism of the α -hydroxypyridines and α -pyridones, or of lactame and lactime condensation in general, is only the old question of amide tautomerism in a slightly different form. Whether in such cases we are dealing with a mixture of two or more tautomeric forms in a condition of equilibrium, or whether one form only is present, is a question not yet satisfactorily answered. One fact, however, seems clearly established, and that is that replacement of the labile hydrogen in such compounds by hydrocarbon radicals materially retards the tendency of one form to pass into the other, and stable derivatives of both types then appear. There thus arise two parallel series of derivatives, in one of which the radical is in union with oxygen, in the other with nitrogen,

¹ Read at the meeting of the New York Section, May 11, 1906.