

the grinding; the finer the powder the more copper is precipitated. The action thus apparently takes place only on the surface of the particles.

The shale removed in one case 95 per cent., in another case the total copper from its solution. The solution remained perfectly neutral, K_2O , MgO , CaO , Na_2O and MnO replacing the copper.

The feldspars orthoclase, albite and microcline, ground in the agate mortar, each remove copper from solution to a surprising extent, 25 grams of the powdered solid taking from 60 to 100 mg. copper out of 50 cc. cupric sulphate solution containing 126 mg. copper. This is a greater precipitation than takes place with kaolin and also greater than that caused by an equal weight of pyrite. Results among different substances are, however, only roughly comparable, owing to the impossibility of getting the powders of the same degree of fineness. The feldspars, originally pure white, were given a decided green tinge by the precipitated copper. After a few washings, further treatment with water removed practically no copper at all from the greenish powder.

Cupric sulphate solution is similar to carbonic acid solution in the extent of its action on feldspar. Somewhat more material was dissolved from orthoclase by 1 per cent. cupric sulphate solution than by suspending in water and passing carbon dioxide for twenty hours. Water alone under similar conditions dissolved but a trace.

Work along the line of that described will be continued in this laboratory.

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

ON AMORPHOUS SULPHUR: III. THE NATURE OF AMORPHOUS SULPHUR AND CONTRIBUTIONS TO THE STUDY OF THE INFLUENCE OF FOREIGN BODIES ON THE BEHAVIOR OF SUPERCOOLED MELTED SULPHUR.¹

BY ALEXANDER SMITH AND WILLIS B. HOLMES.

Some Facts about Amorphous Sulphur Previously Established with More or Less Definiteness.—Insoluble or amorphous sulphur seems

¹ A preliminary paper, including some of the present results, appeared in the *Ber.*, 35, 2992 (1902). The experiments were all made before the work described in the

to have been first isolated, examined and described with some care by Deville.¹ The work of previous observers justifies the following conclusions in regard to this modification of sulphur: It is (1) formed in increasing amounts as the temperature rises, and diminishes in quantity as the temperature once more falls. It is thus (2) generated by an endothermal action from soluble sulphur, and (3) at ordinary temperatures is, therefore, less stable than crystalline sulphur.

The following are briefly the facts which support these conclusions:

(1) Amorphous sulphur can be obtained only when the melted sulphur is chilled rapidly. When heated sulphur is allowed to cool slowly little or no insoluble sulphur is ever found. This fact was shown particularly clearly by a few experiments made by Küster,² and is further supported by many observations described in the present paper.

(2) The higher the temperature at which the sulphur has been held before being quenched the larger, in general, is the proportion of insoluble sulphur obtained. Thus Moitessier,³ in connection with his measurements of the coefficient of expansion of melted sulphur, believing that the variation in the value of the coefficient with change in temperature was due to changes in the proportion of insoluble sulphur present, made a series of estimations of the insoluble sulphur obtainable by quenching from various temperatures. His percentages of insoluble sulphur were as follows:

130°.	145°.	148.6°.	159.9°.	167.4°.	179.4°.	213.5°.	249.9°.	284.0°.	440°.
0	0	2.54	7.03	14.77	22.60	27.09	26.31	29.31	30.27

These data are not quoted in chemical works of reference, and the results of Berthelot's experiments⁴ are more familiar to chemists. Berthelot gives the following table:

Temperature.	130-140°.	155°.	163°.	170°.	185°.	205°.	230°.
Per cent. insoluble sulphur...	None	Trace	Very little	25	29	29	30

preceding paper, No. II (this Journal, **27**, 797), was done. They form a small part of an extensive series made in the effort to discover the reason of the peculiarities in the behavior of sulphur and are for the most part chosen for publication because they bear more or less directly upon the final conclusion in regard to the nature of amorphous sulphur.

¹ *C. R.*, **26**, 117 (1848).

² *Z. anorg. Chem.*, **18**, 365 (1898).

³ *Memoires de l'Acad. de Montpellier*, **6**, 107 (1864); Cf. Smith, Holmes and Hall: "On Amorphous Sulphur. II," this Journal, **27**, 797.

⁴ *Ann. Ch. Ph.* (3), **49**, 481-2 (1857).

These figures are misleading because they give the false impression that there is almost no insoluble sulphur obtainable below 170° , and constant, large amounts about 170° . The work of the present paper (section II) confirms Moitessier's measurements.

(3) The higher the temperature to which the sulphur has been heated the lower, in general, is the temperature at which it freezes. Schaum¹ examined this phenomenon. The work was not done with sufficient thoroughness, however, to justify his inference, *viz.*, that the freezing-point was depressed by dissolved amorphous sulphur by amounts proportional to the quantities of the latter. He observed the freezing-points, simply, and did not simultaneously estimate the insoluble sulphur present. The relation between the temperature of freezing and the amount of dissolved amorphous sulphur was later established conclusively by the quantitative measurements of Smith and Holmes,² and shown to be expressed by Raoult's law. In the light of this relation, now determined, Schaum's observations lead to the conclusion that the higher the temperature to which sulphur has been heated the larger the proportion of insoluble sulphur it contains.

One other fact is, or rather was, generally accepted. It is evidently the opinion of many writers that the increase in the viscosity of melted sulphur, which is so suddenly noticeable near 170° , is coincident with the production of the insoluble form and is due to the presence of the latter. Berthelot even states that larger yields of insoluble sulphur are obtainable by chilling from the temperature of maximum viscosity than from any other temperatures, either higher or lower. We have always found smaller amounts below this temperature and larger ones above it, however, and Kastle and Kelley³ have likewise failed to confirm Berthelot's observation. After we had found that melted sulphur which had been treated with a little gaseous ammonia gave no insoluble sulphur when chilled, but still exhibited the usual increasing viscosity when carried above 170° and resumption of the mobile condition when cooled,⁴ it became doubtful for a time whether there was any connection at all between viscosity and the content of insoluble sulphur. It was only after further investigation, described in the preceding and the present papers, that the existence of the connection was re-established.

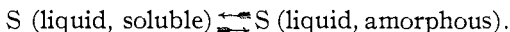
¹ *Ann. Chem.* (Liebig), **308**, 18 (1899).

² *Z. physik. Chem.*, **42**, 469 (1902).

³ *Am. Chem. J.*, **32**, 488 (1904).

⁴ *Ber.*, **35**, 2993 (1902).

The Theory of the Relation of Soluble to Insoluble Sulphur Based on These Facts.—The progressive increase with rising temperature in the proportions of insoluble sulphur, together with the fact demonstrated by the work on the freezing-point that amorphous sulphur can exist dissolved like a foreign body in soluble sulphur, determine one fact about the relation of the two forms. Evidently insoluble sulphur is produced from soluble sulphur by a reversible chemical action and is present, in definite proportions determined by the temperature, in chemical equilibrium with the latter:



This view seems to be held by Küster,¹ Schaum¹ and Duhem,² the last mentioned in a wholly theoretical paper.

Berthelot is the chief exponent of a different theory. He found almost no insoluble sulphur below 170°. Above 170° he isolated from the mass when it had been allowed to harden 30 per cent. of insoluble sulphur. He believed that the values at temperatures above 170° fell short of 100 per cent., only because the cooling had not been sufficiently rapid, and endeavored to obtain larger yields by using (1) a fine stream or succession of droplets of boiling sulphur, (2) cooling in ether and other liquids, (3) immediate extraction of the plastic mass. Adding these refinements in succession he obtained with the first alone 61 per cent., with the first and second 71 per cent., with all three 85 per cent. The material used in the last experiment gave 85 per cent. only when extracted while it was plastic. Next day it gave 47 per cent. and two days later 39 per cent. On these results he based the conclusion that the change from soluble to insoluble sulphur takes place *per saltum* near to 171°.

The work of Moitessier and ourselves shows that Berthelot was undoubtedly seriously in error in finding no insoluble sulphur below 170°. On the other hand, it may well be that 100 per cent. of insoluble sulphur is present not far above 170°, but the discussion in the next paragraph will show that Berthelot's method is incapable of demonstrating either that it is or is not so present.

Plastic and Hardened Amorphous Sulphur and the Reasons for Measuring the Proportion of the Latter Only.—When boiling sulphur is rapidly chilled a transparent, yellow, homogeneous, and perfectly plastic material is formed. Let this be assumed to be a

¹ *Loc. cit.*

² *Z. physik. Chem.*, **23**, 195 (1897).

solution of soluble and insoluble sulphur in certain proportions. It is evidently impossible to determine what these proportions are, for the properties of soluble and of insoluble sulphur in the plastic condition, separately, cannot be determined. The former cannot be obtained in plastic condition at all and we have no means of knowing whether we ever have the latter alone or not.

After the plastic mass has been allowed to become opaque and hard the proportion of insoluble sulphur contained in it is easily determined by extraction. Once this stage has been reached the further transformation of insoluble into soluble sulphur proceeds very slowly indeed and there is little reduction in the proportion of the former at the ordinary temperature, even when the sample is kept for months.¹ The crude method of extracting the plastic threads or beads at once with carbon disulphide, as used by Berthelot, is open to three objections: (1) Amorphous sulphur, both in the soft and in the hardened conditions, being the less stable form at ordinary temperatures, must be ultimately more soluble than crystalline sulphur.² The plastic form must also be more *rapidly dissolved* than is the hardened one. As a matter of fact, in the plastic state sulphur does dissolve pretty freely in carbon disulphide and may be largely recovered by evaporation. (2) The plastic sulphur, when extracted, is found to form an emulsion with the solvent and to be carried in minute drops rapidly through the pores of the thimble. (3) If there is any soluble sulphur present at all it must be covered up by the clinging mass of plastic material and largely escape solution. Berthelot's plan for determining amorphous sulphur in the soft condition is thus wholly futile.

On the other hand, if the transparent, plastic mass is left until it becomes hard, the change is bound to take place in two directions simultaneously. Part of the material, of course, does give quasi-solid, amorphous sulphur. But an undeterminable part must also pass into the soluble crystalline variety. The extraction of the hardened mass does give fairly accurate information in regard to

¹ Deville: *Ann. Ch. Ph.* (3), 47, 94; Smith and Holmes: *Z. physik. Chem.*, 42, 473.

² Doubtless the hardened amorphous sulphur is more soluble, but takes longer than the crystalline variety to reach a state of equilibrium with the solution (see Ostwald: *Handbuch*, 2, 2, 460; Schaum: *Ann.*, 308, 28). Some writers describe plastic sulphur as a distinct, soluble variety of amorphous sulphur (see, for example, Magnus: *Pogg. Ann.*, 94, 308 (1854), and Deville: *Ann. Ch. Ph.* (3), 47, 94). In the plastic condition amorphous sulphur undoubtedly dissolves more *rapidly* but there is nothing to show that it finally dissolves to a greater extent.

The "soluble amorphous sulphur" formed by precipitation will be shown by Mr. R. H. Brownlee in a forthcoming paper to be wholly finely divided, crystalline, rhombic sulphur.

the proportions of the two kinds finally formed, but it gives only a minimum value for the quantity of insoluble sulphur present before hardening began.¹

With the exception of a few trials, therefore, all our measurements were made with the final product of hardening and do not pretend to state how much insoluble sulphur was present, either before chilling or immediately afterwards. They are used only for the purpose of *comparing* the effects of variations in the modes of treatment before chilling and the influences of various foreign bodies. Thus from common sulphur, chilled in ice from 448°, after hardening, we obtained 34 per cent. and no more, of insoluble sulphur. On the other hand, when a few bubbles of ammonia were passed before chilling we obtained from the hardened mass by the same process no insoluble sulphur at all. Again, by distilling the sulphur and quenching the burning stream in ice we obtained, after hardening, 51 per cent. From this it may be inferred that the circumstances attending distillation left the plastic sulphur in such a condition that, during the process of hardening, a smaller proportion of it reverted to the crystalline state. Still again, when 2 per cent. of iodine was added before chilling, the hardened product contained 63 per cent. of insoluble sulphur, the largest yield of this form of sulphur which we were able to secure when, after the cycle of changes attending chilling and hardening, the system had reached a stationary condition. As a rule, in all cases, for the sake of comparison, the product, after chilling, was treated in exactly the same way.

Insoluble Sulphur by Precipitation.—It was only after the ex-

¹ Kastle and Kelley, *Am. Chem. J.*, **32**, 484 (1904), studied the shrinkage which occurs when plastic sulphur hardens. They seem to have assumed that this affords a means of measuring the rate of change of plastic sulphur into *crystalline* sulphur. Thus in one experiment (No. 3, p. 487) they assume in their method of calculation, that the shrinkage represented a complete change from 100 per cent. plastic amorphous sulphur to 100 per cent. solid crystalline sulphur, taking place under water at the ordinary temperature within twenty-four hours. Judging from the results of our experiments, made in a similar way, at least 30 per cent. of insoluble sulphur must still have been present. The change in volume from plastic sulphur with sp. gr. 1.95 to hardened amorphous sulphur with sp. gr. 2.05, however, is practically the same as to rhombic sulphur of sp. gr. 2.06–2.07. Professor Kastle, in a private letter, calls attention to the conviction, expressed clearly in the original paper, that plastic sulphur is composed of several molecularly different kinds of sulphur, all of which are amorphous. He believes that *one* or more of these hardens to insoluble amorphous sulphur, while the *others* give only crystalline sulphur. In his experiments he was endeavoring to trace the history of the latter portion only, on the assumption that the change of volume was due exclusively to the crystallization of this part of the material. The authors do not feel that anything at present known compels us to believe that plastic sulphur contains more than one kind of amorphous sulphur. Nor do they feel that it is safe to assume the absence of any change in volume during even the mere hardening of the supposed uncrystallizable constituent.

periments were made in an entirely different way that specimens containing 100 per cent. of insoluble sulphur were obtained. This was by precipitating sulphur from calcium pentasulphide by means of highly concentrated hydrochloric acid. The pentasulphide was added to the acid in order to secure the constant presence of a great excess of the latter from the start. These experiments were done in collaboration with Mr. R. H. Brownlee, and will form the subject of another paper, which has not yet been completed. They are mentioned here to show that when plastic sulphur—for when first precipitated the sulphur is in fluid droplets—is sufficiently finely divided and is in contact with an active acid, it hardens completely to the amorphous state and none of it assumes the soluble form. A similar fineness of subdivision is evidently impossible of attainment in quenching the boiling liquid. When it had thus been ascertained definitely that the conditions necessary for securing 100 per cent. of insoluble sulphur could not be realized by quenching, the effort further to increase the yield by this method was given up.

The Point of View in Which the Results of the Present Experiments Are To Be Interpreted.—The discussion of the various hypotheses which may be used to explain the results of this work on the supercooling of melted sulphur, so far as such discussion can serve any useful purpose, is given later. Since, however, the results themselves cannot be described clearly excepting in terms of some theory, the one finally adopted is used when necessary throughout the paper. It is based upon consideration of all the results, in the light of the facts given in the preceding paper (II) of the series. Briefly, the explanation of the behavior of sulphur is as follows:

There are two liquid states of sulphur which are partially, but only partially, miscible. These are (1) the pale-yellow, mobile liquid which is the normal form from the melting-point of rhombic sulphur up to 160° , and (2) the brown, viscous liquid which is stable above 160° . These we have styled S_{λ} and S_{μ} respectively. The latter is present in small amount so soon as the sulphur melts, and is formed in increasing proportions as the temperature rises. The proportion is determined by a reversible action $S_{\lambda} \rightleftharpoons S_{\mu}$. At 160° the S_{λ} has become a saturated solution of S_{μ} , the proportion of the latter at this temperature probably not exceeding 12 per cent. When the temperature is raised beyond this point super-

saturation with S_{μ} ensues and a new phase consisting of S_{μ} , in which is dissolved a certain proportion of S_{λ} , arises. According to the phase rule, with one substance, three phases (two liquids and vapor) can coexist only at a definite temperature—the transition point (160°). Hence above 160° only S_{μ} , containing amounts of dissolved S_{λ} which become smaller as the temperature rises, is stable. Rapid heating and the presence or absence of certain foreign substances favor the postponement of the transition of S_{λ} to S_{μ} and lead to the familiar variations in the temperature at which the sudden viscosity first appears. Conversely, rapid cooling from temperatures above 160° , particularly when certain foreign bodies are present, favors the postponement of the transition of S_{μ} to S_{λ} and hinders or prevents almost entirely the occurrence of the change on which an extensive transformation into S_{λ} depends. When conditions are favorable, a large proportion of the S_{μ} may survive to reach the ordinary temperature. The chilled product is then a more or less sticky mass which in time partly reverts to soluble sulphur and partly assumes a quasi-solid, difficultly soluble form. The latter substance is that commonly known as amorphous sulphur. Like all amorphous substances it is a supercooled state of a liquid, namely S_{μ} . The part which reaches the condition S_{λ} gives brittle, crystalline, soluble sulphur when it solidifies.

I. EXPERIMENTAL METHODS.

The sulphur used was purified by recrystallization from pure carbon disulphide in such a way that a fine crystal-meal was obtained. This was pressed free from the mother-liquor, dried at a gentle heat, and preserved in a loosely corked bottle. Specimens from the same lot were used in each series of similar experiments. Except when otherwise stated 25 grams formed the charge of each tube. The heating to some definite temperature was conducted in open tubes. A large glycerol bath was used for lower temperatures, a paraffin bath for higher ones, diphenylamine vapor at 310° and sulphur vapor at 448° . The supercooling was effected by rapidly pouring the sulphur, or by breaking the tube into powdered ice. Other methods had been found to give yields which were no larger, and were often smaller and always less regular. The experiments on freezing-points¹ had shown that once the temperature had fallen to about 115° the reversion

¹ *Z. physik. Chem.*, **42**, 472.

of the dissolved amorphous sulphur to soluble sulphur was comparatively slow. Thus, since the cooling sulphur was not allowed to form large masses, only a few seconds elapsed before the lowering in temperature requisite to arrest reversion had been attained. When the proportion of amorphous sulphur was small, the product became hard in a few hours and the amount of insoluble sulphur found by extraction closely corresponded to the amount which had actually been present before the chilling began. The freezing-point experiments, which involved amounts from zero up to 5.5 per cent., show that the results were literally quantitative within that range. When, on the other hand, a high temperature had been used, the supercooled mass was often of the familiar elastic description. In such cases the hardening occupied two days or more and, although 30-63 per cent. of insoluble sulphur was contained in the final product, the total amount of S_{μ} in the material at the plastic stage, not to speak of the liquid before the cooling began, must have been much greater (see preceding paragraph). This uncertainty, and the further fact that a longer time must have elapsed before 115° was reached and the danger of reversion to the soluble form was past, makes caution necessary in the interpretation of the data in regard to sulphur supercooled from very high temperatures. These data are used, therefore, only for comparing the effect of variables other than temperature itself.

Except where otherwise stated, the supercooled mass, after it had become hard, was pulverized and passed through a fine sieve, in order to secure uniform physical condition in the samples used for extraction. The solvent employed was carbon disulphide. Comparable results were obtained by using equal weights (10 grams) in the same state of subdivision and removing the soluble sulphur each time by the same number of fillings (five) of a Soxhlet extractor. The extractions were made in duplicate in each case. Correction for the quantity of insoluble sulphur dissolved at the same time was made as described in the previous paper, where also the experiments testing the accuracy of this method of estimating amorphous sulphur are described.¹

II. RESULTS OF SUPERCOOLING ORDINARY SULPHUR, THAT IS, SULPHUR WHICH HAS ACQUIRED TRACES OF SULPHUR DIOXIDE, OR SULPHURIC ACID, BY EXPOSURE TO THE AIR.

Each of the results given below was obtained by taking the aver-

¹ *Z. physik. Chem.*, **42**, 474.

age of three or four experiments. Preliminary experiments showed that three hours were required for the attainment of the maximum proportion of insoluble sulphur at the lower temperatures. The individual observations varied in a most disturbing manner, the highest showing sometimes 0.5 per cent. of insoluble sulphur more than the lowest. The results at 448° showed exceptional irregularity, the individual percentages¹ being 31.8, 36.6, 36.1, 31.8. This variation could not be removed by stirring or any other expedient so long as common sulphur was used alone. Trial showed that two tubefuls of sulphur taken from the same lot, heated side by side for the same length of time and cooled simultaneously in the same manner, sometimes gave percentages of amorphous sulphur 0.5 apart. The same experimental method was found to give concordant results in other series, *e. g.*, that in which iodine was present (section IV). The results, which are represented graphically in Fig. 1 (section IV), were as follows:

Temperature.	130°.	140°.	150°.	160°.	170°.	180°.	200°.	220°.	240°.	310°.	448°.
Per cent. insoluble sulphur.....	4.2	5.6	6.7	11.0	18.7	22.5	27.0	29.4	33.0	32.6	34.1

In the above experiments the sulphur entered the bath cold. It was thought that the equilibrium values could be better defined by making another series of experiments in which the sulphur should first be heated for a considerable length of time at a temperature 20° above that of the experiment, so as to create an excess of amorphous sulphur, and be then placed in the bath. At 150° the results were in close correspondence, *viz.*, with cold sulphur 6.7 per cent., with sulphur which had been two hours at 160° previous to being placed in the bath at 150°, 6.8 per cent. At 170°, however, the sulphur which had been two hours at 200° gave 17.4 per cent., while the result with cold sulphur was 18.7. At other temperatures similar discrepancies were encountered.

It will be seen that the above results, taken as a whole, give nothing more than a general idea of the relative proportions of amorphous sulphur obtainable from common sulphur by the use of different temperatures. The values up to 160° also doubtless give a fairly accurate notion of the proportions of S_{μ} present in solution in the S_{λ} up to the transition point at which saturation with S_{μ} occurs.² They dispose at once of Berthelot's belief that

¹ Deville, *C. R.*, **26**, 117, gives 34 per cent., which is the exact mean of our results.

² Schaum suggested (*Ann.*, **308**, 23) that if the amounts of amorphous sulphur present at various temperatures were known, Van't Hoff's formula, $\frac{d \ln K}{dT} = -\frac{q}{RT^2}$, might be

practically no amorphous sulphur exists below 170° . They also render very improbable his conclusion that the amounts of it are constant above 170° and that throughout the lower part of the region $170-448^{\circ}$ it constitutes the whole of the material. The divergence from Moitessier's results given in the introduction is doubtless due in part to the sensitiveness of the behavior of sulphur to the influence of traces of impurities, the nature and amount of which must vary in different samples, and in part to the fact that he used very small samples for extraction.

III. AMORPHOUS SULPHUR NOT OBTAINABLE BY SUPERCOOLING WHEN THE SULPHUR DIOXIDE OR SULPHURIC ACID IS REMOVED.

In the earliest experiments made to determine the time required for the production of the maximum yield of insoluble sulphur, although the results were by no means regular, it was observed, especially at the higher temperatures, that there was a distinct falling off from the maximum amounts in the tubes which had been longest heated. It was thought that some action of the air was accountable for this, and the point was reserved for later investigation.

Later it was noticed that freshly recrystallized lots of sulphur gave abnormally small yields, and their use was therefore avoided in the experiments described so far.

When the former idea was tested by passing air through sulphur heated at 448° the yield of insoluble sulphur was found to be as large as usual, no matter how long the stream of air continued. Carbon dioxide, on the other hand, when used simply to displace the air in the tube, reduced the yield below 5 per cent. Its effect was the same when it was allowed to pass through the melted sulphur. Taking all these facts together, it seemed probable therefore that sulphur dioxide or sulphuric acid formed by slow oxidation was in some way responsible for the whole phenomenon of the formation of the amorphous sulphur, and that the removal of the impurity by the use of carbon dioxide, recrystallization, or otherwise, inhibited the production of insoluble sulphur. The

used for the calculation of the heat of formation of the amorphous body. Since Van't Hoff's formula depends on the application of Avogadro's hypothesis to gases or dilute solutions, it could not be expected to give results of any value for a system containing only the two liquid participants in the equilibrium $S_{\lambda} \rightleftharpoons S_{\mu}$ and no diluent. As a matter of fact the results of the calculation applied to the above data are quite erratic.

following paragraphs give a selection of the experiments which confirmed and enlarged this conclusion.

Sulphuric Acid Present in Sulphur.—When sulphur which has been exposed to the air is washed with water, a small amount of sulphuric acid is easily detected in the washings. This fact is familiar to all chemists¹, and was confirmed by trial in the case of the sulphur employed in these experiments. The quantity varies from 0.0025 per cent. upwards to about 0.02 per cent. When sulphur is heated bubbles of gas appear in it and, according to Frankenheim², are reabsorbed when it cools. Malus holds this gas to be sulphur dioxide.

To ascertain the outside limit of the amount of sulphur dioxide contained in amorphous sulphur, a rough quantitative experiment was made. Pure amorphous sulphur was used. Carefully dried carbon dioxide, which was led over heated copper to remove free oxygen, was passed through the sulphur at 150-160°. The issuing gas entered a Liebig bulb apparatus containing bromine water, to absorb any reducing gas. Plugs of glass wool were inserted to retain any particles of free sulphur which might be transported with the gas. The sulphuric acid found in the Liebig apparatus was determined. The amount of amorphous sulphur taken was 62.5 grams. This gave 0.07 gram of sulphur dioxide. As some oxidation of the sulphur by the carbon dioxide undoubtedly occurred, and some sulphur vapor was doubtless carried over, even this small amount is in excess of the amount of sulphur dioxide originally in the amorphous sulphur.

Products of Supercooling when the Sulphur Dioxide is Removed by Prolonged Heating, Heating in Vacuo, Recrystallization, and Washing.—The per cent. of amorphous sulphur after various modes of treatment was as follows:

	Heated 8 hours.	Heated 1½ hours.
At 448°, open tube.....	2.6	34.0
At 220°, open tube.....	25.6	29.5
At 220°, 12-15 mm. pressure.....	11.9	...
At 200°, open tube.....	25.8	27.0
At 180°, open tube.....	20.0	22.5

¹ See Norman Leonard: *Analyst*, **26**, 319 (1901); abstract in *J. Chem. Soc.*, **82**, ii, 131 (1902).

² *J. prakt. Chem.*, **16**, 12 (1839); Malus, *Ann. Ch. Ph.* (7), **24**, 574 (1901), observed a large volume of gas and noted that after escape of the bubbles and resolidification of the sulphur, heating reproduced an equal amount of fresh gas. This was repeated forty-five times with the same specimen! Surely the air which penetrates the mass after the shrinkage following crystallization and remains entangled when the material is remelted was mistaken by him for freshly formed gas.

At temperatures below 180° , with the open tube, the effect of prolonged heating, if there was any, was too small to be distinguished with certainty.

Sulphur, recrystallized in a fine meal from carbon disulphide, heated for two hours in a steam-bath to free it from the solvent, with no precautions to exclude the air, and then immediately heated for one and a half hours at 448° in an open tube, gave only 10.1 per cent. When precautions were taken to exclude the air, the amount of insoluble sulphur was below 1 per cent.

Recrystallized sulphur which had been exposed to the air for weeks was very finely powdered and washed repeatedly with boiled water to remove the product of oxidation. It was then washed with alcohol and ether, and placed in a steam-bath for thirty minutes, the air having access to it during the *whole* proceedings. After being heated for one and a half hours at 448° in an open tube it gave only 11.3 per cent. of insoluble sulphur.

In all these cases the sulphur was brown and viscous above 160° and yellow and mobile below it, as usual.

The Work of Malus on the Viscosity of Sulphur.—In a paper¹ published in December, 1901, while the present work was in progress, Malus describes a systematic and extensive series of experiments, and shows that the production of viscous sulphur by cooling the heated element rapidly to 100° or to 15° is determined by the presence of sulphur dioxide, and that in the absence of the dioxide the cooled product is mobile at 100° and brittle when solid. The points in his paper with which we are at present concerned are as follows:

“A narrow tube full of sulphur *plunged suddenly* into a bath at 100° , after being heated for *ten to fifteen minutes* at 357° , has these properties: (1) reddish yellow tinge, (2) surface highly invaginated, (3) great viscosity, (4) rate of crystallization when inoculated with a monoclinic crystal, two minutes for first centimeter, (5) sudden cooling to 15° gives a soft solid. This liquid he calls S_1 . Reheating at any stage gives S_1 again.”

“Sulphur *plunged suddenly* into a bath at 100° , after being *three hours* at 357° , has these properties: (1) pale-yellow color, (2) no invagination, (3) mobility, all but a superficial layer 7-8 mm. deep which is viscous (after ten hours at 357° often completely mobile even at surface), (4) rate of crystallization to monoclinic

¹ *Ann. Ch. Ph.* (7), **24**, 491-571.

sulphur five and a quarter seconds for first centimeter, (5) suddenly cooled to 15° , either directly from 357° or after being intermediately at 100° , the product is brittle. This liquid he calls S_2 . Reheating at any stage gives S_2 again, and not S_1 ."

"Sulphur cooled *slowly* to 100° , after being *ten to fifteen minutes* at 357° , resembles S_2 excepting that when reheated it gives S_1 . He calls this S_2 ."

"Using 310° (instead of 357°), even with more than twelve hours' heating, the change into S_2 is not always complete."

"At 185° , even 105 hours do not quite suffice to bring the speed of crystallization up to that of S_2 ."

"At 357° a stream of carbon dioxide for ten to twenty-two minutes, or even the mere insertion of glass rods for five minutes, cause complete transformation into S_2 . This effect he explains by supposing that these agents assist in the liberation of the bubbles of gas whose retention gives viscous sulphur (S_1). At 310° , with glass rods, forty minutes are required to give S_2 . At 185° , 160 hours are needed. Sulphur dioxide does not produce S_2 . On the contrary, when it was passed into S_2 , S_1 is formed."

While amorphous or insoluble sulphur is nowhere mentioned in the paper, the interpretation of his results can easily be made out if we make an assumption, for which, however, no basis is to be found in his paper. This assumption is that viscosity and the presence of amorphous sulphur are related to one another as effect and cause. The final result of our own work shows that this assumption is justifiable. The appearance of his paper while our work was in progress in fact brought welcome confirmation of observations which were in some cases difficult to accept.

Since the presence of our S_{μ} undoubtedly causes the viscosity of sulphur rapidly cooled to 100° or to 15° , it may now be inferred from Malus's paper that heating at 357° for three hours destroys the capacity of the S_{μ} to be supercooled. At 310° twelve hours, and at 185° 105 hours, are barely sufficient for the same purpose. In each case it is the gradual escape of sulphur dioxide at the surface which permits the change to take place. A stream of carbon dioxide or the presence of glass rods accomplishes the same result by helping the liberation of the gas. Unless the sulphur dioxide is reintroduced the sulphur remains incapable of giving a viscous product containing amorphous sulphur.

Products of Supercooling when Sulphur Dioxide Is Removed or De-

stroyed by Certain Gases and by Alkalies.—As we have seen, the normal amount of amorphous sulphur found after heating at 448° for one and a half hours is 34 per cent. In the following experiments, except where otherwise stated, the same temperature and time were used.

Carbon Dioxide.—Carbon dioxide, washed with water, was passed down to, but not under, the surface of the sulphur. The yield was only 4.5 per cent. When the gas actually passed through the sulphur the yield was the same. A very slight dark deposit was found inside the delivery tube near the exit in all experiments with carbon dioxide. It was probably carbon, produced by a slight reduction by the hot sulphur. Thus, with this gas the presence of sulphur dioxide is not completely excluded.

Nitrogen.—Dry nitrogen gas, passed over heated cupric oxide, and traversing the sulphur, gave only 4.7 per cent.

Ammonia.—When dry ammonia was passed through sulphur at 448° for one hour and a half no amorphous sulphur whatever was found in the product. The action here is doubtless in part chemical, since ammonia interacts with sulphur dioxide. The product had a slight odor of ammonium sulphide.

Hydrogen Sulphide.—Dry hydrogen sulphide passed in the same way gave 0.85 per cent. Here again interaction must occur.

Sulphur Vapor.—Since it appeared that the action of these gases was in large part mechanical, the effect of sulphur vapor itself was tried. Sulphur was boiled vigorously in an open tube for two hours, and, on extraction, was found to contain only 13.2 per cent. of insoluble sulphur. Sulphur vapor was therefore less effective than carbon dioxide or nitrogen.

Alkalies.—A little powdered potassium hydroxide placed in the sulphur at 448° prevented entirely the formation of insoluble sulphur. It is known that sulphur containing the amorphous form, when allowed to stand in an alkaline solution, loses a large proportion of the latter¹. We found that finely powdered sulphur originally containing 54.7 per cent. of insoluble sulphur, after being allowed to stand in a 5 per cent. solution of sodium carbonate for several days, contained only 8.1 per cent.

Temperatures below 448° .—At temperatures below 448° the effect of gases passing for one and a half hours was observed.

The following are a few of the results:

¹ Berthelot: *C. R.*, **44**, 318, 378.

Temp.	Gas.	Per cent. insol. sulphur.	
		Found.	Normal amt. at same temp.
310°	carbon dioxide	6.2	32.5
240°	carbon dioxide	29.1	33.0
160°	carbon dioxide	11.8	11.0
140°	ammonia	0.0	5.5

It appears that purely mechanical means have no perceptible effect below 180°, but that substances capable of interacting chemically can act at any temperature to destroy the possibility of obtaining insoluble sulphur.

Air at 448°.—Undried air passed through sulphur for two hours gave 34.5 per cent. of insoluble sulphur. Dried air passed for eight and a half hours gave 30.8 per cent. These results are not different from those without air, similar variations having been found when no air was used, but show that the *disappearance* of insoluble sulphur by long heating does not occur when air is employed.

Restoration of the Capacity to Give Insoluble Sulphur by Exposure to the Air and by Use of Sulphur Dioxide.—The capacity once more to yield insoluble sulphur is not recovered by solidification, but it returns gradually during prolonged exposure in a finely powdered condition to the air. One specimen, after treatment with carbon dioxide at 448°, was allowed to solidify and *next day* was heated for two hours at 160°. It gave only 3.2 per cent. (instead of 11). Another, after an hour had been allowed for solidification and loss of all carbon dioxide by diffusion, gave, when once more heated at 448°, only 2.2 per cent. Still another, after solidification, allowed to remain in the tube exposed to the air (but in a compact mass) for twelve days, gave, when heated at 448°, 12.1 per cent. (instead of 34).

A specimen treated with carbon dioxide, and, after solidification, recrystallized from carbon disulphide and quickly freed from the solvent in a steam-bath, gave, when once more heated at 448°, only 1 per cent.

In all cases leading sulphur dioxide through the specimen at 448° for a few minutes completely restored the normal yield of insoluble sulphur. Leading air through the mass for an hour and a half produced the same effect. It thus appeared as if the amorphous body could be produced and destroyed any number of times by the alternate use of suitable substances. The following are a few of the results at 448°:

	Per cent.
1. Dry carbon dioxide.....	4.5
2. Dry carbon dioxide, then dry air.....	31.2
3. Dry carbon dioxide, then dry sulphur dioxide.....	36.5
4. Dry carbon dioxide, then recrystallization.....	1.0
5. Dry carbon dioxide, then recrystallization, then dry air....	32.9
6. Dry carbon dioxide, then dry air, then carbon dioxide.....	4.9

Best Method of Preparing Sulphur Which Cannot be Supercooled and Yields no Insoluble Sulphur.—It may be inferred from the above experiments that perfectly pure sulphur would give no amorphous sulphur when heated for an hour and a half at 448° . The best way to prepare sulphur closely approaching this ideal is to make it in small quantities, as it is needed, by treatment with ammonia at 448° , recrystallization from pure carbon disulphide to remove traces of ammonium sulphide, and rapid drying in a steam-bath. Sulphur prepared in this way and used at once gives almost no insoluble sulphur, however it may be heated.

The Freezing-Point of Pure Sulphur.—Two samples of the above sulphur were melted without special avoidance of overheating and their freezing-points were determined with the Beckmann thermometer. The freezing-points were 119.170° and 119.165° respectively. Subsequent extraction showed a barely visible quantity of insoluble sulphur. These measurements agree well with the freezing-point of pure sulphur, 119.25° , formerly¹ obtained by extrapolation.

IV. OTHER SUBSTANCES WHICH FAVOR SUPERCOOLING OF S_{μ} .

Effects of Chlorine, Bromine and Their Hydrides.—All these experiments were made at 448° . The hydrogen chloride and hydrogen bromide were dried and led through the sulphur. For the sake of comparison the chlorine and bromine were *both* carried in a stream of dry carbon dioxide.

Hydrogen Chloride.—This gas increased the yield of insoluble sulphur (38.6 per cent.) and prolonged heating after the stream of gas was stopped and the tube opened to the air did not greatly affect the result (35.4 per cent.). One experiment was made to ascertain whether, when *the cooling is slow* the adjustment to a condition of equilibrium, which causes the insoluble sulphur to disappear, is disturbed by hydrogen chloride. Only 0.8 per cent. of insoluble sulphur was found.

Hydrogen Bromide at 448° .—This gas gave 34.9 per cent.

¹ *Z. physik. Chem.*, **42**, 476.

Chlorine at 448°.—Dry chlorine gas gave 56.8 per cent. The product was comparatively liquid and sticky, without any elasticity, and took many days to become hard.

Bromine at 448°.—As it seemed likely that the large yield in the case of chlorine had been caused partly by interaction between a chloride of sulphur and the water used in cooling, the material in this case was cooled by pouring over the bottom of a dry metal pail standing in a freezing-mixture. Part of the product was ground in a mortar with chloroform to remove any bromide of sulphur, which by interaction with the moisture from the air might have added to the yield of insoluble sulphur, and was then extracted. It gave 38.22 per cent. A good deal of insoluble sulphur had remained unhardened and ran in droplets through the thimble used in the extraction and was lost. The rest of the product was treated with chloroform, and then freed from this solvent and ground up with carbon disulphide. When this had evaporated the product was pulverized and extracted. The yield in this way was 65.1 per cent.

Another portion was cooled slowly. If the presence of a bromide of sulphur had contributed to the above large yield the same influence would have been noticed, probably on a more extensive scale, in a slowly cooled specimen. The product, which was brittle when cold, was rubbed with chloroform and was afterwards extracted in the ordinary way. The yield was 1.1 per cent, so that the large yield above was independent of any action of moisture on a bromide of sulphur.

Restoration of the Capacity to Give Insoluble Sulphur by Hydrogen Chloride, Sulphuric Acid and Phosphoric Acid.—It was naturally anticipated that the above substances would also restore the capacity to give insoluble sulphur, and it was found that they did so. Even dried finely powdered metaphosphoric acid, when introduced in small amount, had the same effect. In this case subsequent treatment with carbon dioxide did not once more destroy the capacity to give insoluble sulphur, the phosphoric acid being non-volatile. The following are typical experiments, all made at 448°:

	Per cent.
Hydrogen sulphide, then dry hydrogen chloride.....	43.3
Carbon dioxide, then metaphosphoric acid.....	31.0
Carbon dioxide, then hydrogen chloride.....	44.3

In the last two experiments special care was taken to purify the carbon dioxide from free oxygen by passage over heated copper. These two experiments in particular show conclusively that the normal amount of insoluble sulphur can be formed when sulphur dioxide is almost absolutely excluded. The amorphous sulphur can therefore hardly be a chemical compound of sulphur with sulphur dioxide, since it can equally well be formed by the help of other bodies like metaphosphoric acid and hydrogen chloride.

That the restoration occurs also at lower temperatures was determined by experiment. Thus one specimen of sulphur was kept at 140° and treated first with ammonia to remove the capacity to give insoluble sulphur, and then with a few drops of concentrated sulphuric acid. Thorough mixing was secured by continuous use of a stirring apparatus. The amount of insoluble sulphur was 5.30 per cent., the proportion given by ordinary sulphur at this temperature.

In another experiment made in the same way at 140° , with continuous stirring, an effort was made to determine also the time required for the restoration. Sulphuric acid and powdered metaphosphoric acid were compared, the vessels being present simultaneously in the same bath. Samples were taken out of each and chilled and extracted separately. It was found, however, that in both cases the first sample, taken after ten minutes, gave as much insoluble sulphur as the later ones. The maximum amount with the former agent was 5.77 per cent. and with the latter 5.79 per cent. This reaction speed, which is shown by preliminary experiments¹ to be much greater than that proper to ordinary sulphur, was especially surprising when the general inactivity of phosphoric acid and its vanishingly small solubility in melted sulphur were considered.

Effects of Iodine; Preliminary Experiments.—Since iodine had been found by Dietzenbacher² to confer unusually persistent plasticity upon supercooled sulphur it was expected that by its use larger amounts of insoluble sulphur would be obtained. Powdered iodine dissolves rapidly and in large amounts in melted sulphur. The solution is deep reddish brown in color. Except where otherwise stated, we used two parts of iodine to one hundred of sulphur. These solutions gave off a little iodine vapor, but the loss of iodine

¹ Not yet published.

² *C. R.*, 56, 39 (1863).

was inconsiderable, even during one to two hours at the higher temperatures.

It was determined that rubbing the chilled, viscous mass immediately with carbon disulphide, allowing the solvent to evaporate, pulverizing the residue and leaving it for two days to solidify completely gave somewhat larger yields of insoluble sulphur when iodine was present than did the method used in earlier experiments. This modification of the former method¹ was therefore here substituted for the mere spontaneous hardening. It had the additional advantage that nearly all the iodine evaporated with the carbon disulphide and the powdered sulphur was but slightly colored by a trace of iodine remaining.

As the yields of insoluble sulphur were uniformly larger than with any other substance except bromine, it was thought, as before, that this might be due to interaction between an iodide of sulphur and the water used for cooling. Berthelot states² that the chloride and bromide of sulphur give larger proportions of insoluble sulphur by the action of water than any other mode of precipitation. It was found, however, that none of the amorphous sulphur was due to this cause. The so-called "iodide of sulphur" was prepared by Guthrie's method³ and used as if it had been a supercooled mass. After treatment exactly like that used in the regular experiments the residue was extracted. It gave no insoluble sulphur. This conclusion was confirmed in another way. Sulphur was heated with 2 per cent. of iodine at 448° for one and a half hours and was then allowed to cool slowly in the large iron tube. While the insoluble sulphur thus had an opportunity to disappear in the usual manner any iodide of sulphur which might be present or might be formed during the cooling was bound to remain. Treatment of the residue in the usual manner, however, did not yield even a trace of insoluble sulphur. Preliminary experiments having shown that all results with iodine were much more regular and consistent than with sulphur dioxide, a more extensive and systematic series of experiments was made with this substance.

¹ In the work described in sections II and III this modification made no difference in the yield and most of the experiments in which it was used have therefore been omitted (see, however, section V).

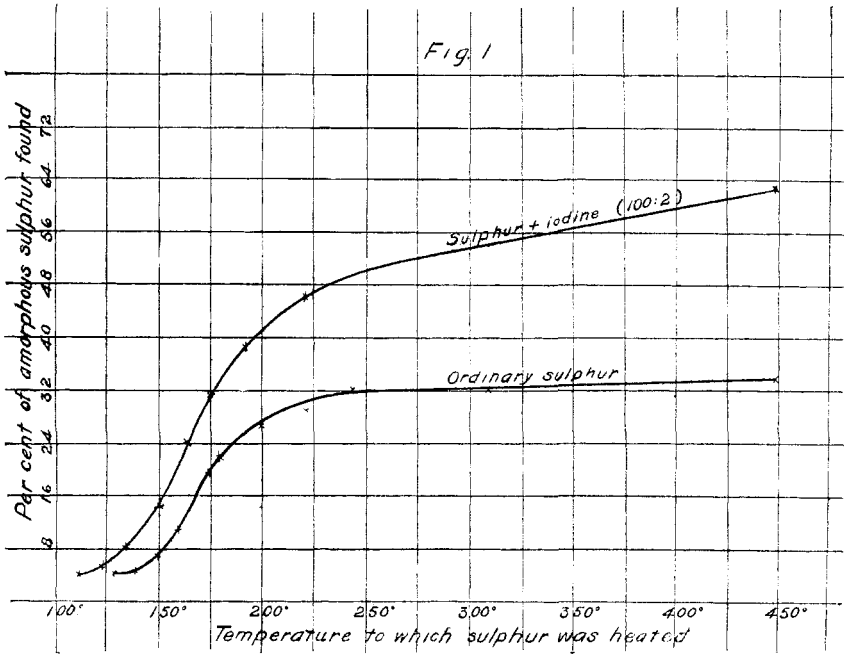
² *Ann. Ch. Ph.* (3), 49, 482.

³ McIvor, *Chem. News*, 84, 5 (1902), finds the so-called moniodide to be a solid solution and not a compound. The fact that it gave no amorphous sulphur by the above treatment seems to support this view. Boulough, *C. R.*, 136, 1577, finds that sulphur and iodine give a eutectic mixture melting at 65.5° and no compound.

The Results with Two Parts of Iodine to One Hundred of Sulphur.—At the temperatures from 120° to 310° (see following table) two tubes previously held for two hours at a temperature from 10-15° higher were placed in the same bath with two cold tubes and the four were kept at the temperature of the bath (column 1) for two hours. At 110° two tubes previously kept at 125° alone were used, as this preliminary superheating was necessary to melt the sulphur. At 448°, on the other hand, the equilibrium point was reached from below only, as a higher temperature than 448° could not be obtained without the use of more than an atmospheric pressure. In the following table the numbers in the second and third columns are the means of the four results of extraction (two samples of the content of each of two tubes). The individual results did not in any case differ from the mean by more than 2 per cent. of the amount of the insoluble body. As will be seen, the proportions of amorphous sulphur formed with rising and with falling temperature correspond more closely than did the results of experiments without iodine.

Temperature.	Per cent. insoluble sulphur.		Mean.
	Equilibrium from below.	Equilibrium from above.	
110°	4.05	4.0
120°	5.33	5.35	5.3
135°	8.60	8.61	8.6
150°	13.44	14.14	13.8
165°	23.76	24.51	24.1
175°	31.59	31.50	31.5
190°	37.81	38.21	38.0
220°	46.73	47.26	47.0
310°	53.70	54.61	54.2
448°	62.64	62.7

In Fig. 1 these results are exhibited graphically (temperature horizontally and per cent. of insoluble sulphur vertically), together with the results in the absence of iodine (section II). The latter, on the lower curve, are uniformly much smaller. The lowness of the amount at 310° on the upper curve is due to the fact that, while at 448° the tube on immersion in ice and water bursts violently and a minute dispersion and complete cooling of the sulphur is instantly produced, at 310° the temperature is not high enough to bring about this result and intimate and immediate contact is more difficult to secure. At lower temperatures the reversion of the insoluble sulphur is less rapid and therefore the effect of slower contact with the ice must be less conspicuous.



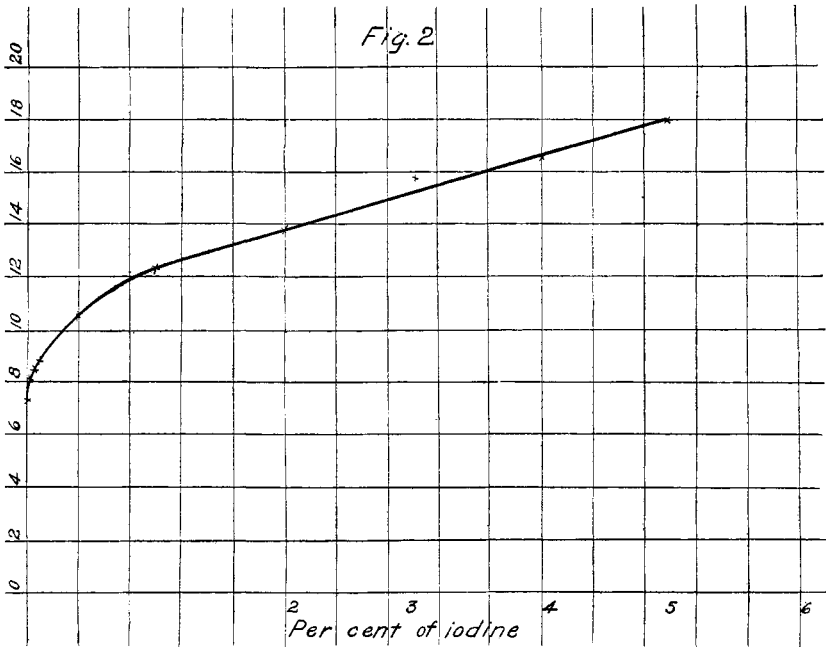
Results with Varying Proportions of Iodine at 150°.—The following table shows the marked effect which increasing amounts of iodine produce at the same temperature. All the experiments were done simultaneously in the same bath. Twenty-five grams of sulphur were used in each of them, as in each of the preceding experiments. The quantities of iodine are parts with one hundred of sulphur.

Iodine.	0.	0.07.	0.04.	0.1.	0.4.	1.	2.	3.	4.	5.
Per cent. insoluble sulphur.....	6.7	8.16	8.38	8.90	10.52	12.26	13.79	15.85	16.47	17.86

The graphic representation of these results (Fig. 2), in which the quantity of iodine is plotted horizontally and that of insoluble sulphur vertically, seems to show that from 1 part of iodine onwards the increase in the amount of insoluble sulphur is approximately proportional to the amount of iodine.

V. OTHER METHODS OF SUPERCOOLING AND OF TREATING THE SUPERCOOLED MASS.

Another Method of Treating the Supercooled Product.—In view of Berthelot's statement above quoted, an attempt was made to ascertain the effect on the yield of various modifications in the



treatment. Since the sticky amorphous sulphur is freely dissolved by carbon disulphide, but may be largely recovered in insoluble form by evaporation¹, it seemed probable that a preliminary rubbing in a mortar with the solvent and removal of the latter by evaporation would forestall considerable reversion to the soluble form. To test this question together with that of the effect of varying lengths of time for solidification, a large quantity of sulphur was heated at 448° for two hours, and then poured into ice in a thin stream. The product was divided into six portions, with the following treatment and results:

	Per cent. in- soluble sulphur.
1. Extracted ordinary way after two days.....	36.6
2. Extracted ordinary way after six days.....	36.1
3. Treated by evaporation at once and pulverized and extracted immediately.....	30.8
4. Treated by evaporation at once and pulverized and extracted three days later.....	32.3
5. Treated by evaporation after two days and then pulverized and extracted.....	27.8
6. Treated by evaporation after six days and then pulverized and extracted.....	35.9

¹ Cf. Berthelot: *Ann. Ch. Ph.* [3], 49, 476.

The results show that with common sulphur our regular method of allowing several days for solidification and then pulverizing and extracting give the largest yield.

Supercooling by Quenching Burning Sulphur.—More sudden cooling can be achieved by distilling the sulphur in a fine, burning stream from a retort (placed 50 cm. above a vessel of ice and water). In this way the sulphur is kept near to its boiling-point until it actually enters the water in a rapid succession of beads. In the set of experiments made in this way a test was also made of the influence of acids on the cooled product.

	Per cent.
1. Soft beads extracted at once (uncorr.).....	58.8
2. Soft beads treated by evaporation, pulverized and extracted at once.....	51.3
3. Product after six days pulverized and extracted.....	40.0
4. Soft beads seven days under strong nitric acid, pulverized and extracted.....	30.6
5. Soft beads six days under strong sulphuric acid, pulverized and extracted.....	33.2
6. Distilled with 2 per cent. iodine, treated by evaporation, pulverized and extracted after one day.....	52.1
Another single experiment similar to 2:	
2 ₁ . Soft beads treated by evaporation, pulverized and extracted at once.....	51.1

No. 1 has no claim to trustworthiness, as the beads ran together in the extractor and the carbon disulphide did not reach the inner part of the material. On the other hand, some liquid insoluble sulphur formed an emulsion with the solvent and was lost. No. 3 corresponds to No. 2 of last set, and shows an increased yield by the new method of chilling. No. 2 corresponds to No. 3 of last set and shows a greatly increased yield by combined use of the new methods of chilling and treating the supercooled mass. The long stream of sulphur was heated in an atmosphere of sulphur dioxide produced by the combustion, and the soft beads were saturated with the same substance and therefore were perhaps still subject to its influence after they were cold. Apparently, under these circumstances the treatment of the chilled mass by rubbing with carbon disulphide does markedly increase the yield. The chilling of a burning stream raises the yield from 34 per cent. to 40 per cent. (No. 3) and the evaporation process adds 11 per cent. more (Nos. 2 and 2₁). In No. 6 the combined influence of iodine and distillation was tried. In this case it was found that the small

amount of iodine remaining in the material after it had been treated by evaporation and pulverized caused a gradual increase in the yield of insoluble sulphur. Another portion of the material from No. 6 was extracted three days later and gave 52.1 per cent., while a third portion extracted thirteen days later still contained 52.6 per cent. This effect is interesting in connection with the retardation of the rate of hardening which Kastle and Kelley¹ observed when plastic sulphur was kept under decinormal iodine solution. Contrary to Berthelot's statement² we found in the above and other experiments that keeping the soft product under acids gave no greater yields than other ways of treating the same material. A much finer condition of subdivision, such as that secured by precipitation, is necessary in order that the acid may be effective.

Supercooling by Means of Ether.—Finally, cooling with ether, which in Berthelot's hands gave the largest yields, was tried. The sulphur was boiled in a tube drawn out to a capillary at the bottom. By breaking this capillary and applying pressure on the surface of the sulphur by means of a foot-blower, the material was rapidly forced out in a fine jet into a vessel of ether surrounded by ice and salt and situated at the bottom of a pail filled with carbon dioxide gas to prevent accidental inflammation. The sulphur formed minute beads and could not well have been chilled more suddenly. The product was treated by evaporation with carbon disulphide and pulverized and extracted at once. It gave 44.4 per cent. insoluble sulphur. While the yield was in excess of the largest obtained from ordinary sulphur by cooling with ice, it is considerably smaller than that given by the distillation experiments in which perhaps the liberal supply of sulphur dioxide is the determining cause of the difference. Berthelot's 85 per cent. was from a distillation experiment, in which sulphur dioxide intervened, and he extracted the soft material at once. This experiment has been criticized already.

¹ *Am. Chem. J.*, **32**, 489.

Ann. Ch. Ph. [3], **49**, 484.

VI. COMPARISON OF THE BOILING-POINTS AND SPECIFIC GRAVITIES OF SPECIMENS OF SULPHUR WHICH RESPECTIVELY DO AND DO NOT YIELD INSOLUBLE SULPHUR, WITH A VIEW TO ASCERTAINING WHETHER THESE TWO KINDS OF SULPHUR ARE ACTUALLY OF THE SAME OR OF DIFFERENT CONSTITUTION NEAR THE BOILING-POINT.

The fact that insoluble sulphur lowers the freezing-point of melted sulphur shows definitely that insoluble sulphur comes from the solidification of a modification of sulphur which is distinct from soluble sulphur and can exist in solution in melted sulphur, at all events near to its temperature of solidification. The experiments described thus far in this paper *seemed* to show that this distinct modification could be destroyed and reproduced at will. It was inadmissible to suppose that the gases which appeared to effect its removal and reproduction acted simply as catalytic agents. Such agents may affect the speed of an action, but cannot afterwards alter the proportion natural to a state of equilibrium.¹ The subsequent withdrawal of a mere catalytic agent does not diminish the amount of the product, as seems here to be the case when the sulphur dioxide is driven out. At all events these statements apply strictly in all cases where the introduction of the catalytic agent and its withdrawal are not accompanied by the performance of any work. In the present instance it is impossible that, by the introduction of gases or mere glass rods, work could have been done in amount even remotely approaching that required to accomplish such extensive displacements of the equilibrium point. On the other hand, the hypothesis that amorphous sulphur is a compound of soluble sulphur with some other substance or substances is equally difficult to accept. The molecular proportion of sulphur dioxide is very minute and other bodies may take its place, giving the same product. The idea that the insoluble modification could be really altered in amount by foreign bodies was therefore given up.

The alternative view is that once the maximum amount at a given temperature has been reached, the proportion of the insoluble modification is not affected by leading gases, for example ammonia and sulphur dioxide, alternately through the mixture. The explanation of the appearance or non-appearance of insoluble sulphur would then have to be sought in some influence

¹ Ostwald: *Handbuch*, 2, 2, 262.

which the foreign body exerted at some stage of the operation of cooling. An attempt to test this alternative was made at the boiling-point and at two temperatures somewhat below 448° . It is a question of determining whether two liquids, one of which does and the other does not *give* at least 34 per cent. of a distinct substance, differ as markedly in physical behavior as two such liquids would do if only one of them *actually contained* this amount of a foreign material. The boiling-points and specific gravities were the properties which could be most easily compared. A rough calculation showed that 30 per cent. of a non-volatile body of molecular weight equal to that shown by the freezing experiments to be proper to dissolved amorphous sulphur (S_{∞}), should have elevated the boiling-point by an amount of the order of 10° - 20° . Unless insoluble sulphur had exactly the same vapor pressure as soluble sulphur at 448° some difference in the boiling-points should have been observable, provided always the specimens compared were not identical in constitution. Even if the vapor-pressures happened to be identical at 448° , they would not be so also in a partial vacuum at 406° . The actual comparison described below showed that, both at atmospheric pressure and under somewhat reduced pressure, the boiling-points were identical, and that at 448° and at 302.5° the specific gravities were alike.

These facts, together with others detailed in the preceding paper, led therefore to the conclusion that the gases and other substances affected the sulphur during the process of cooling only, and at some temperature considerably below the boiling-point.

The Boiling-point of Sulphur and Its Relation to Insoluble Sulphur.—A quantity of recrystallized and redistilled sulphur was placed in a wide tube, surrounded by asbestos cloth to reduce the loss of heat by radiation and convection. The bulb of a thermometer, filled with nitrogen under pressure and graduated up to 550° , was immersed in the boiling material. After half an hour the reading became steady at 437.2° . Sulphur dioxide was then passed in slowly for three hours, during which the reading did not change. Then dry carbon dioxide was led into the sulphur for one hour without any alternation in the boiling-point of as much as 0.1° being observed. Then ammonia was used for an hour and the reading remained exactly 437.2° . That the instrument was in working order was shown by the fact that when a more rapid stream of one of the gases was allowed to enter, the bubbles of the

cold gas striking the bulb of the thermometer immediately produced a slight fall in the reading. But the original temperature was recovered as soon as the speed of the gas was diminished.

Under somewhat reduced pressure the constancy of the boiling-point could not be maintained so perfectly, even while no gas was being introduced. The readings, at intervals of three to ten minutes, were as follows, the symbol interposed indicating that ammonia or sulphur dioxide was introduced at that point: 405.6°, 405.6°, 405.7°, (NH₃), 405.8°, 406.0°, 405.7°, 405.7°, (SO₂), 405.7°, 405.8°, 405.9°, (NH₃), 405.9°, 405.9°, (SO₂), 406.0°, 405.9°, (Se), 407.2°, 407.2°, 407.0°.

To show that actual presence of a foreign solute *did* elevate the boiling-point, 1.025 grams of selenium¹ was added at the point indicated. This produced an immediate elevation of 1.2°. The weight of sulphur used was about 81 grams.

The Specific Gravity of Liquid Sulphur and Its Relation to Insoluble Sulphur.—The specific gravity of liquid sulphur was determined with the utmost care at the temperature of diphenylamine vapor and at that of sulphur vapor. Sulphur which had been recrystallized and twice distilled was employed. At each temperature two measurements were made, one with the sulphur in its natural condition, the other with sulphur through which ammonia had been passed. Glass bulbs, with short exit tubes, holding 15-20 cc. were used as pycnometers. They were completely filled with the liquid sulphur, and the expansion when they were lowered into the bath caused the excess of sulphur to overflow. The volumes of the bulbs and the coefficient of expansion of the glass were determined by calibration with mercury between 0° and 100°. The results were as follows, the first column (I) under each temperature giving the data for the specimen of natural sulphur, and the second (II) those for sulphur treated with ammonia.

	Diphenylamine vapor: 302.5°.		Sulphur vapor: (448°?).	
	I.	II.	I.	II.
Weight of mercury filling pycnometer				
at 0°, in grams.....	228.868	267.850	267.850	267.850
Volume at 0°, in cubic centimeters... .	16.835	19.701	19.701	19.701
Volume corrected to temperature....	16.982	19.874	19.957	19.957
Weight of sulphur.....	28.876	33.742	31.981	31.916
Specific gravity of sulphur.....	1.697	1.697	1.602	1.593

¹ From the heat of vaporization of sulphur at 448°, namely 362, a rough estimate of the molecular weight of selenium in solution in sulphur may be made from the above data. The value corresponds to the formula Se₃₄.

Coefficient of expansion of the glass, 0.000029.

Specific gravity of mercury at 0°, 13.5956.

The substantial agreement of the pairs of specific gravities, as well as of the pairs of boiling-points, seem to justify the conclusion that there was no difference in constitution at 300-448° between sulphur which did and sulphur which did not give insoluble sulphur.

VII. COMPARISON OF THE SOLUBILITIES OF SULPHUR WHICH DOES AND SULPHUR WHICH DOES NOT GIVE INSOLUBLE SULPHUR, WITH A VIEW TO ASCERTAINING WHETHER THESE TWO KINDS OF SULPHUR ARE ACTUALLY OF THE SAME OR OF DIFFERENT CONSTITUTIONS BETWEEN 119.25 AND 160°.

The results of the experiments on the boiling-point and specific gravity showed that in the region between the transition point (160°) and the boiling-point the amorphous sulphur was present in solution in sulphur whether it could be obtained by sudden cooling or not. It remained to ascertain whether amorphous sulphur was similarly present under all circumstances in liquid sulphur below 160°. Since below 160° amorphous sulphur is the less stable form it should be more soluble than melted crystalline sulphur. If, therefore, sulphur which has been treated with ammonia really contains no amorphous sulphur, while that which has been treated with sulphur dioxide does contain from 4 to 12 per cent. of the less stable modification, there should be a difference in the solubilities of the two kinds in a substance like triphenylmethane. Moreover, the difference in solubility observable should be exaggerated by the fact that the solution of the amorphous sulphur will displace the equilibrium by which it is related to the soluble material and so lead to the continual restoration of its natural concentration in the sulphur phase until the organic solvent is saturated with it.

This question was put to the test by preparing solutions containing known concentrations of sulphur and triphenylmethane. Ammonia and sulphur dioxide were led through the solutions for thirty to sixty minutes, and after the treatment with each gas the temperatures at which the solutions became cloudy through separation of sulphur were determined repeatedly. Constant temperatures of saturation were easily found. The results were as follows:

Amount of S with 10 grams CH(C ₆ H ₅) ₃ .	Temperature of saturation.	
	After SO ₂ .	After NH ₃ .
11.43	138.5	138.3
15.71	143.0	143.0

These points lie close to the curve given in the preceding paper¹ and there was no difference between the solubilities of the two kinds of melted sulphur. From this it may be inferred that the sulphur phases which separated contained identical proportions of dissolved amorphous sulphur. Of course when the solutions were suddenly cooled, only those containing free sulphur dioxide showed any amorphous sulphur in the hardened product. With the others this product was brittle and crystalline from the first, the amorphous sulphur having reverted to the soluble form during the chilling.

VIII. DISCUSSION OF THE RESULTS.

All Specimens of Sulphur Have the Same Constitution at Identical Temperatures when They Have Reached a Condition of Equilibrium.

—The experiments described in section VI show that specimens of sulphur which, respectively, do and do not give insoluble sulphur are identical in constitution when they have reached a state of equilibrium at temperatures near to the boiling-point. These specimens all contain the same proportion of the liquid which, when supercooled, gives amorphous sulphur. Again, the absence of any displacement of the transition point at 160° (see preceding paper, "On Amorphous Sulphur, II," sections II, III and V) leads to the same conclusion for all specimens of sulphur which are in a condition of equilibrium at that point. Similarly the experiments described in section VII of this paper lead to this conclusion for different specimens of liquid sulphur throughout the range of temperatures between the freezing-point and the transition-point (119.25 to 160° .)

It is only at the freezing-point itself, when liquid sulphur passes into solid, monoclinic sulphur, that a difference seems to assert itself. The first paper of this series shows that the liquid from which insoluble sulphur can be obtained by chilling freezes at various temperatures, all below 119° . The experiments in section IV of this paper, on the freezing-point of pure sulphur, show that specimens which give no insoluble sulphur freeze close to 119.25° . This difference between specimens which do and do not give insoluble sulphur is only apparent, however. It must be remembered that the specimens employed in the determination of freezing-points in the work of the first paper were not in a condition of equilibrium. They were obtained purposely by rapid cooling from higher tem-

¹ *Loc. cit.*

peratures. The longer they were kept before being placed in the freezing apparatus the more nearly they approached in freezing-point the samples treated with ammonia of which use was made in this paper.

Thus the study of liquid sulphur stage by stage from the boiling-point to the freezing-point shows conclusively that all specimens of sulphur, when they have reached a condition of equilibrium at identical temperatures, have the same constitution. It shows that, whether when chilled they give insoluble sulphur or not, they all contain definite proportions of the form which, if it can be supercooled, yields insoluble sulphur. It shows that the proportion of amorphous sulphur depends only on the temperature.

The Nature of Amorphous Sulphur.—At the freezing-point amorphous sulphur is clearly a third variety and not one of the two, namely, solid-monoclinic and melted-soluble sulphur (S_λ), which are directly concerned in the transition. This is clear, because when present it displaces this transition point. It is equally evident that amorphous sulphur is not a third variety, but is itself one of the two liquids, namely, S_λ and S_μ , whose transformation constitutes the transition at 160° . This is evident because its presence does not displace this transition point. The conclusion is therefore reached that amorphous sulphur is supercooled S_μ .

The fact that it is amorphous, and must therefore be a supercooled liquid of some kind, is in harmony with this conclusion. That 100 per cent. of S_μ cannot be secured in the hardened condition is evidently due to partial reversion to the soluble form in the plastic mass. We have shown that when proper conditions are realized, as during precipitation, this reversion may be entirely prevented.

In view of the above conclusion it is clear that even minute traces of foreign bodies influence strongly the capacity of S_μ to become supercooled. They evidently exercise this influence during the chilling process. Apparently those which, like ammonia and hydrogen sulphide, cause the production of no insoluble sulphur do so only by destroying the sulphur dioxide which would otherwise have the opposite effect. This is evident because recrystallization and immediate use give the same result as leading in ammonia, and inability to be supercooled is therefore a property

of pure S_{μ} . Sulphur dioxide and iodine, on the other hand, favor in some way the supercooling of S_{μ} .

At What Stage and in What Way Do Foreign Bodies Influence the Supercooling of S_{μ} ?—At least three answers to these questions are possible.

(1) The foreign body may retard the backward progress of the action $S_{\lambda} \rightleftharpoons S_{\mu}$ (possibly, but not very probably, by destroying something which if present alone would hasten it) and so diminish the speed with which the chemical equilibrium adjusts itself in response to the rapid changes in temperature attending the operation of chilling. This sort of influence, if exerted at all, will be exerted throughout the whole range of temperatures and stages from the boiling-point until hardening is complete.

(2) The foreign body may play no part until the transition from the liquid to the hardened condition is in progress, and at that time may determine the formation of the insoluble sulphur.

(3) The foreign body may exert its influence at the transition point from S_{μ} to S_{λ} (160°), favoring perhaps the supersaturation of S_{μ} with S_{λ} , or hindering the initiation of the new phase of which S_{λ} is the chief constituent. A fact which repeatedly forced itself upon our attention in the work described in the preceding paper shows that this supposition touches closely what is probably the true explanation of the greater part of the influence of foreign bodies. We have seen that distilled sulphur does not show the absorption of heat or the onset of viscosity so sharply as do the other kinds. Apparently the formation of the new phase which marks the upward transition does not so readily take place with sulphur prepared under the conditions attending distillation. It may, therefore, be presumed that the inverse change from S_{μ} to S_{λ} brought about by cooling will be similarly less prompt with distilled sulphur. Now it has been shown by Berthelot¹ and by ourselves (section V) that, when no foreign ingredient has been purposely introduced, this kind of sulphur is precisely the one which gives by chilling the largest yields of insoluble sulphur.

There are probably still other possible modes in which the results may be brought about, and, in any case, it is not likely that any one kind of influence operates alone. Thus, in section V the influence of iodine in continuing to increase the proportion of insoluble sulphur after hardening is complete has been demonstrated.

¹ *Ann. Ch. Ph.* [3], 49, 482.

Yet if (2) were the sole cause it would be difficult to see why previous heating at various different temperatures should give different proportions of insoluble sulphur.

A considerable amount of experimental work along the lines just indicated, as well as in other directions which there has been no occasion to mention in these papers, has already been done. It is hoped that a part of this will be sufficiently advanced for publication within a short time.

Analogy in the Behavior of Iron and Steel.—In conclusion it may be pointed out that the problems raised in this work are of especial interest in view of their similarity to those encountered in the study of the chilling of iron and steel. The similarity may be indicated by two examples taken from an almost endless number that might be used. Pure iron (α -ferrite) passes into β -ferrite at 765° and into γ -ferrite above 890° . In this last condition it is non-magnetic. These temperatures are transition points similar to 95.6° and 160° for sulphur, save that in the case of iron both lie within the region in which the material is solid. When chilled, γ -ferrite promptly reverts to α -ferrite and recovers its magnetic qualities. The addition of 12 per cent. of manganese, however, so reduces the facility with which γ -ferrite passes into β - and α -ferrite that when the alloy is chilled the product contains only supercooled γ -ferrite and is wholly non-magnetic. Even when cooled very slowly or when kept for hours at 400 - 500° the specimen passes with difficulty into a condition of equilibrium by changing into an alloy of manganese with α -ferrite. This is an example of a foreign body hindering a transition which involves the production of a new phase. Again, Charpy and Grenet¹ have shown that silicon favors the separation of graphite in cast iron, facilitating the initial appearance of the carbon phase and causing the separation to proceed more rapidly after it has been initiated, while at the same time affecting in no way the amount finally deposited when the system has reached a condition of equilibrium. Here a foreign body seems to assist a process involving the production of a new phase. Our view is that the phenomena of supercooling shown by sulphur and by iron are to be explained on the same principles.

RESULTS OF THIS INVESTIGATION.

(1) The hardening of plastic sulphur is discussed and it is shown

¹ C. R., 134, 103.

that partial reversion to soluble sulphur prevents the securing in quasi-solid form of the whole of the amorphous sulphur present. It is stated, however, that sulphur formed by precipitation in presence of concentrated acids does yield 100 per cent. of insoluble sulphur and that only the impossibility of realizing the requisite condition of very fine subdivision is, therefore, responsible for the smaller yields from melted sulphur which has reached the highest temperatures previous to being chilled.

(2) A new series of measurements of the proportions of insoluble sulphur formed when common sulphur is chilled from various temperatures is given. The amounts vary from 4.2 per cent. at 130° to 34 per cent. at 448° . In this and all other cases described, only the insoluble sulphur which remains after the viscous material has completely hardened is estimated.

(3) It is shown that when sulphur is subjected to prolonged heating at 448° , or is heated for a shorter time *in vacuo*, or is used immediately after recrystallization, or is washed with water before being heated, the amount of insoluble sulphur obtainable by chilling is greatly reduced. The effect of these modes of treatment seems to be to remove a trace of sulphuric acid which sulphur acquires by exposure to the air.

(4) It appears that gases like carbon dioxide and, particularly, ammonia and hydrogen sulphide, when led through melted sulphur destroy the ability to give insoluble sulphur. Their use does not, however, affect the viscosity above 160° .

(5) It is shown that air and sulphur dioxide restore the ability to give insoluble sulphur. The halogens, the halogen hydrides, and even phosphoric acid have the same effect.

(6) It is found that sulphur which has been treated with ammonia while melted and has afterwards been recrystallized, if used at once, freezes at 119.17° and contains no insoluble sulphur.

(7) Sulphur containing iodine (100 : 2) gives, when heated and chilled, large amounts of insoluble sulphur. These range from 4 per cent. at 110° to 62.7 per cent. at 448° .

(8) The increase in the amount of insoluble sulphur obtained at 150° is approximately proportional to the quantity of iodine present when the quantity of the latter is 1 per cent. or more.

(9) Sulphur prepared by distilling the element and quenching the burning stream in ice water gives 51 per cent. of insoluble

sulphur. Chilling boiling sulphur in ether gives 44.1 per cent. of the insoluble form.

(10) It is shown by identity in boiling-points under ordinary and reduced pressures and identity in specific gravities that sulphur which will give the insoluble form when chilled is identical in constitution near the boiling-point with that which will not.

(11) It is shown by identity in solubility between 120° and 160° that the two kinds of sulphur mentioned in (10) are identical in constitution also below the transition point of S_{μ} to S_{λ} (160°).

(12) The facts referred to in (10) and (11), together with the conclusions of the preceding paper showing the identity of the two kinds of sulphur at the transition point (160°) itself, demonstrate that the insoluble form is present in all specimens of melted sulphur in proportions depending upon the temperature alone, whether by treatment with ammonia or otherwise they have lost the capacity to give insoluble sulphur by chilling or not.

(13) The conclusion is reached that amorphous sulphur is supercooled S_{μ} —the form stable above 160° .

(14) With pure sulphur, freed from sulphur dioxide by recrystallization or by treatment with carbon dioxide above 310° , or by treatment with ammonia or hydrogen sulphide at any temperature at which it is fluid, the S_{μ} reverts so rapidly to the soluble form that it cannot be supercooled. When traces of sulphur dioxide, iodine and other substances are present, S_{μ} is more or less completely supercooled and gives amorphous sulphur. The way in which the latter class of foreign substances produces this effect is still being investigated.

(15) The close analogy of these phenomena to those observed in the cooling of cast iron and steel is pointed out.

THE BASIC PROPERTIES OF OXYGEN: COMPOUNDS OF ORGANIC SUBSTANCES CONTAINING OXYGEN WITH NITRIC, SULPHURIC AND CHLOR- SULPHONIC ACIDS.

BY D. MCINTOSH.

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THE basic properties of organic compounds containing oxygen have been discussed in a number of articles,¹ and the quadrivalence

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