

We have been using this method for the nickel determination long enough to discover the weak points, if there were any, and are perfectly satisfied with the results. Failure on the part of our students is a very rare thing, although we have greatly cut down the amount of nickel in our unknowns. I think we are safe in saying that the test for nickel is fully as delicate as that for cobalt; and the ease and rapidity with which it is carried out make it the best method, in our estimation, we have ever used.

ON PRECIPITATED SULPHUR.¹

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Historical.—Ever since, in the year of 1848, Deville² first discovered amorphous sulphur and Selmi³ found the same substance in flowers of sulphur, many chemists have studied its occurrence and its properties. St. Claire Deville⁴ examined numerous specimens of commercial flowers of sulphur and found that the percentage of the insoluble amorphous modification varied from 11.3-23.4 per cent. In roll sulphur he found 2.9-7.3 per cent. of sulphur insoluble in carbon disulphide. Deville⁵ was the first to notice that the sudden cooling of melted sulphur gave sulphur insoluble in carbon disulphide. After sudden cooling of sulphur from 230° Berthelot's⁶ method of measurement⁷ gave 60 per cent. of the amorphous variety. After pouring the hot sulphur into ether his method of extraction gave 70 per cent. After heating the sulphur with a small quantity of iodine and cooling suddenly in water, the method used seemed to indicate the presence of as much as 80 per cent. of amorphous sulphur.⁸

Berthelot⁹ also prepared amorphous sulphur by precipitation from various compounds of sulphur by means of acids and other reagents. He says¹⁰ "In general the kind of sulphur disengaged is independent of the agent used for precipitating, provided it is not an alkali or an oxidizing

¹ The work upon this paper was carried on simultaneously with that published by Smith, Holmes and Hall, *Journal of the American Chemical Society*, **27**, 797, 979, and was read in abstract by Alexander Smith on June 30, 1906, at Ithaca, N. Y., before the American Chemical Society.

² *Pharm. Centr.*, **1848**, 200; Graham Otto's "Lehrbuch," **1**, 538.

³ Graham Otto's "Lehrbuch," **1**, 539.

⁴ Graham Otto's "Lehrbuch," **1**, 539.

⁵ *Compt. rend.*, **26**, 119; Ostwald's "Lehrbuch," **2**, 2, 551.

⁶ *J. pr. Chem.*, **71**, 360.

⁷ In the experiments referred to, Berthelot did not allow the precipitated sulphur to harden, but extracted the viscous mass with carbon disulphide immediately. It is evident that much of the sulphur could not come in contact with the solvent, and hence a high percentage of amorphous sulphur would be indicated.

⁸ *Compt. rend.*, **56**, 39.

⁹ *Ann.* (3) **49**, 430.

¹⁰ *loc. cit.* p. 444.

agent, and that its activities are exercised rapidly without notable heat formation."

He concluded that the state of combination of the amorphous sulphur in the original compound alone regulated the proportion of amorphous sulphur, and that negative sulphur is precipitated completely soluble, and positive sulphur completely insoluble in carbon disulphide. For instance a sulphide should invariably give soluble sulphur and sulphur dioxide insoluble amorphous sulphur. In the same paper, however, he states that the amounts of amorphous sulphur obtained from a given amount of sodium thiosulphate when treated with acids varies with the conditions. Weber¹ observed that by treating potassium polysulphides with very dilute nitric acid he obtained sulphur of which only 86 percent was soluble in carbon disulphide, thus not confirming the observations of Berthelot.

It has been possible to substantiate the observations of Weber, and further to show that the kind of sulphur disengaged from a given compound is not independent of the precipitant. Cloez² thought that sulphur was precipitated from solutions in soluble or insoluble form, according to whether it separates from alkaline or acid solution. While many researches have been carried out upon sulphur, the statements with reference to precipitated sulphur seem to be conflicting, and no one, up to this time, has studied the precipitation of sulphur under definite conditions.

Then, too, the work of Alexander Smith and his collaborators³, has elucidated the relations of the two forms of liquid sulphur, the yellow mobile S_{λ} (rhombic sulphur) and the brown viscous S_{μ} insoluble in carbon disulphide (so-called amorphous sulphur), and has therefore prepared the way for a more exact and instructive study of precipitated sulphur. The formation of S_{μ} by precipitation in various reactions at or below the ordinary temperature, and therefore in a metastable condition, is a subject of especial interest in the light of the above mentioned conclusions.

Accordingly at the suggestion and under the direction of Professor Alexander Smith of the University of Chicago, I undertook the study of precipitated sulphur with the purpose of investigating the relation between the proportion of amorphous sulphur (S_{μ}) found in a given sample of precipitated sulphur and the conditions under which the precipitation and hardening of the sulphur took place. In connection with this, it was hoped that an improvement could be made in the formulation of the facts attempted in the rules of Berthelot and Cloez.

In order to obtain a general knowledge of the various actions in which

¹ Watts Dict. of Chem., old edition.

² Dammer, 4, 207.

³ This Journal, 797.

sulphur is precipitated and to ascertain which conditions influence the proportion of insoluble sulphur and to what extent they influence it, an extensive series of preliminary experiments was made. In Section I a selection of these is given. In Section II the final experimental method is described. In the two following sections, the results in the reactions subjected to exact study are detailed, viz. Section III, the interaction of bromine and iodine, with sulphides and polysulphides; Section IV, the interaction of acids with sodium thiosulphate.

Finally, in Section V, the particular conditions which determine the production and proportion of amorphous sulphur (S_{μ}) are discussed.

General Features of the Precipitation. To understand what follows, the general phenomena presented by most of the precipitations must be noted. When the reagents are mixed, a very pale, almost white cloudiness appears in the liquid, either immediately, or, when dilute solutions are used, after a brief interval. The cloud is almost always composed at first of fluid droplets, whether the product is ultimately found to contain insoluble sulphur or not. The emulsion settles, and, after the lapse of several hours, or days, the precipitate becomes hard and brittle.

In some instances, the hardening takes place without any change in the form of the material, in other instances, notably when the action has taken place in less concentrated solutions, the droplets flow together forming an oily liquid, and when considerable percentages of insoluble sulphur are produced, the droplets fuse together giving a viscous mass.

The Methods.—In order to be able to analyze the sulphur according to the method we adopted it was necessary after the precipitation of the sulphur, to allow it to harden, so that it could be obtained in powdered form.

In the case of sulphur precipitated from sulphides, this was attended with no difficulty, but with the sulphur precipitated from sodium thiosulphate by acids or by the interaction of sulphur dioxide and hydrogen sulphide, the case was different. Usually the sulphur was precipitated as minute droplets which soon united to form a very viscous mass that in some cases required more than a week before becoming hardened, and in the meantime it was rapidly oxidized by air. To avoid this difficulty, the sulphur was rapidly freed from most of the moisture by pressing between folds of filter paper, or by spreading upon a dry plate. This viscous or sticky and damp product was then ground in a mortar with acetone (a substance miscible with water) and carbon disulphide, and the mixture was allowed to evaporate to dryness. In this way a hard material could be obtained in a fraction of the time usually required in the absence of this special treatment. In order to facilitate the removal of the vapors of the liquid, and at the same time to exclude the air, the filter paper or dry plates on which the material had again been spread were placed over sul-

phuric acid in a dessicator through which a stream of dry carbon dioxide flowed continuously.

In order to study the problem it was, of course, necessary to determine the percentage of amorphous sulphur formed, in each case, and the method employed was that improved by Smith and Holmes¹. This method consists in (1) grinding the hardened sulphur in a mortar, (2) sifting through a fine sieve and (3) extracting with carbon disulphide.

Owing to the fact that in some of the experiments it was difficult to prepare any considerable quantity of precipitated sulphur, it was decided to employ five grams for each extraction, (instead of ten,) as used by Smith and Holmes².

To test the accuracy of the method when five gram quantities were employed, sulphur containing the amorphous variety was precipitated. After the plastic sulphur hardened it was ground in a mortar, sifted through a fine sieve and extracted. In each case the carbon disulphide overflowed the extraction apparatus five times. That the method was capable of giving concordant results is shown by the following data:

Experiment	Per cent Amorphous Sulphur
1	23.58
2	23.55
3	23.70
4	23.45

Sources of Possible Error.—There seem to be two sources of possible error in this method. First, (a) the solubility of amorphous sulphur in carbon disulphide, and second, (b) possibility of diminution of the proportion of amorphous sulphur during or after solidification.

(a) *Correction for Solubility of Amorphous Sulphur.*—The first possibility of difficulty, the solubility of amorphous sulphur in carbon disulphide, under the conditions of these experiments, could be disposed of only by proper correction. The amorphous sulphur required for the purpose was prepared by precipitating sulphur from sodium thio-sulphate by means of concentrated hydrochloric acid, and submitting this product after hardening, to a treatment in which extraction with carbon disulphide, pulverization and sifting through a fine sieve were repeated several times, in order that entire removal of the soluble variety might be assured. The entirely soluble precipitated sulphur necessary was prepared by the precipitation of sulphur from calcium polysulphide, by means of dilute hydrochloric acid. Then a series of mixtures was prepared by mixing intimately various proportions of the two kinds of sulphur.

The solubility was determined under the same conditions to which the material was exposed in the main experiments. In each case five grams

¹ Z. physik. Chem., 42, 469.

² loc. cit.

of the sulphur to be extracted was weighed into a thimble made from filter paper that previously had been extracted with carbon disulphide. The thimble was placed in a Soxhlet extraction apparatus and the carbon disulphide allowed to overflow five times.

In the following table the first column gives the percentage of amorphous sulphur originally introduced, the second the quantity of amorphous sulphur left after extraction of five grams of the mixture, with five fillings of carbon disulphide and the third the percentage of amorphous sulphur which had been dissolved.

Per cent. of amorphous sulphur in the mixture	Weight of amorphous sulphur left from five grams	Per cent. of amorphous sulphur dissolved, calculated on basis of total sulphur
10	0.492	0.16
20	0.985	0.30
40	1.970	0.60
50	2.462	0.75
80	3.940	1.20
100	4.925	1.50

Inasmuch as the most careful mixing of the ingredients could not give so complete a dissemination of the amorphous sulphur in these artificial mixtures as probably existed in the mixtures produced by precipitation, it is likely that the solubilities appearing in the table are somewhat smaller than those which natural mixtures of the same concentration would have shown. The amounts added by way of correction to the quantities of amorphous sulphur actually found by extraction were therefore probably somewhat too small.

The curve¹ (Fig. 1) puts the data in a form in which they may be used for the correction of observations. The percentages of amorphous sulphur found are laid off along the ordinate and the corresponding percentages of the amorphous sulphur dissolved, (calculated upon the basis of total sulphur) along the abscissa. Thus, the percentage to be added to the percentage of amorphous sulphur found, in each specimen, could be read directly from the curve. These corrections have been applied to all the results given and the final results are expressed in percentages of amorphous sulphur thus shown to be present in the precipitated sulphur.

(b) *Possibility of Diminution of the Proportion of Amorphous Sulphur During and After Solidification.*—In the second place, the percentage of amorphous sulphur (S_u) might diminish perceptibly during the time which necessarily elapsed between the precipitation and the accomplishment of the hardening of the sulphur.

The question whether the proportion of insoluble sulphur found in the

¹ Smith and Holmes, *Z. physik. Chem.*, 42, 469, plotted the weight of amorphous sulphur left in ten grams of the mixture against the weight of amorphous sulphur dissolved.

final product of hardening represented the amount actually formed by the interaction and present in the plastic material when first precipitated is discussed in Section V. That the loss of S_{μ} by reversion after solidification,

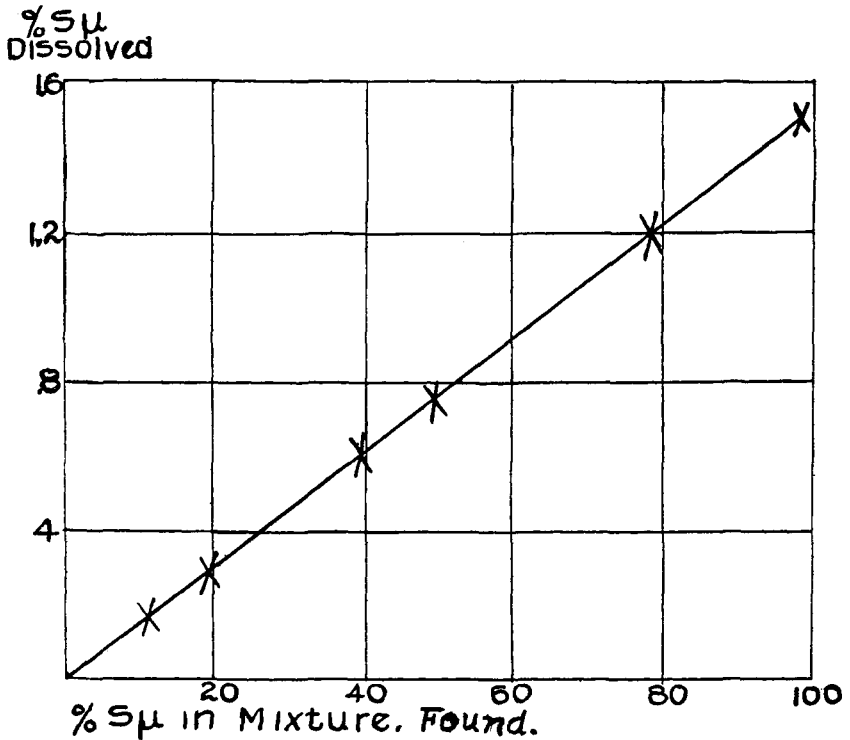


FIG. 1.

makes little progress during even months of waiting has been shown by Berthelot¹, Deville², Smith and Holmes³, and by the results of our own experiments.

I. Preliminary Experiments

Sulphur is precipitated in a number of reactions, but some of these, such as the interaction of sulphur monochloride with water, in consequence of the immiscibility of the materials, do not lend themselves to the maintenance of definite concentrations or fixed temperatures during the action. In other cases, such as the decomposition of polythionates, the yields of sulphur are too small. Most of these preliminary experiments, therefore, were made with four actions: *viz.*, that of sulphurous acid and hydrogen sulphide (par. 1 below) that of polysulphides with acids (par. 2 below), that of sulphides with bromine and iodine (par. 4 below), and that of

¹ Compt. rend., 4, 313, 378.

² Ann. chim. phys., (3) 47, 94.

³ Z. physik. Chem., 42, 469.

sodium thiosulphate with acids (par. 5 below). It will be seen later that even of these four, only the last two were subjected to the most complete quantitative investigation.

1 *Sulphur from Interaction of Sulphurous Acid with Hydrogen Sulphide*.—The sulphur obtained by saturating water successively with sulphur dioxide and hydrogen sulphide, did not quickly become pulverulent. On the contrary, it was very viscous and was also rapidly oxidized by the air. When this sulphur was allowed to stand for eight days, or until thoroughly hardened, the average composition was 79 per cent. S_{μ} and 21 per cent. S_{λ} . After the more rapid hardening process, by grinding with carbon disulphide and acetone, and drying in absence of air, the average proportion of S_{μ} was 82.6 per cent.

In these experiments the concentration of the interacting substances varied extensively during each experiment, and differed greatly in different experiments. The experiments are mentioned, therefore, simply because the result is interesting in view of the familiar nature of the action. The maintenance of constant concentrations during the interaction for example, by mixing solutions of the gases, involved the use of such enormous volumes of liquid, in order that sufficient amounts of the product might be secured, that further study of this action was not undertaken.

2. *Sulphur from Interaction of Polysulphides With Acids*.—Calcium polysulphide was prepared according to the method described in Graham Otto's "Anorganische Chemie." Freshly slaked lime was boiled for several hours with flowers of sulphur and after cooling, the solution was filtered. By this means, a 2.5 normal solution of calcium polysulphide was prepared. A solution of sodium polysulphide of approximately equivalent concentration was prepared by boiling the pure commercial sodium sulphide with flowers of sulphur. In these experiments, the acids were added to separate portions of the polysulphide solutions. The following table shows the concentration (2.5 normal) and composition of the polysulphide, the nature of the acid, and the proportion (corrected) of insoluble sulphur found:—

Polysulphide	Acid used and its quantity	% S_{μ}
2.5 N Ca S_x	Acetic, 33 percent., in excess	0.0
" "	" glacial, in excess	0.0
" "	Hydrochloric, 6 N, solution still alkaline.	0.0
" "	" 6 N, in excess	0.8
" "	" 12 N, " "	2.4
2.5 N Na ₂ S ^x	" 6 N, " "	0.5

In each of the above cases an almost pure white powder was precipitated. When the order of mixing was reversed and the polysulphide was added to the acid, hydrogen polysulphide was formed. It is seen from the above results that sulphur containing a measurable, though quite small, content of the insoluble variety may be precipitated from a polysulphide by using an excess of acid.

3. *So-called "Soluble" or "Soft" "Amorphous Sulphur" and Its Properties.*—The sulphur formed from polysulphides is often described as "soluble amorphous sulphur",¹ and is thereby distinguished from soluble rhombic or monoclinic sulphur, on the one hand, and from insoluble amorphous sulphur on the other². This sulphur is indeed almost white, instead of yellow but that is evidently a result of fine subdivision. Professor J. P. Iddings, whom we desire here to thank for the interest he shows in the problem, was kind enough to examine this sulphur with the polarizing microscope. When first precipitated, this sulphur consists of minute fluid globules³ which are wholly isotropic. While they are being watched they become crystalline without altering noticeably their spherical form. At this stage each globule is composed of a mass of elongated crystals radiating from the center of the sphere, each part of the mass showing extinction and illumination independently of the other parts, as the sphere is rotated by turning the stage. While these phenomena are being observed, the whole globule, still without altering its spheroidal form, suddenly turns into a single, transparent, homogeneous crystal with four positions where extinction takes place throughout the whole sphere simultaneously.

The substance after hardening is therefore not optically amorphous at all, although, so far as could be seen with a magnifying power sufficient to show the other phenomena with perfect distinctness, the form is perfectly spherical. This so-called soluble amorphous sulphur (from polysulphides) is consequently nothing but rhomboid sulphur⁴. If, as seems probable, the substance thus passes through the fluid and the monoclinic crystalline stages, both at the temperature of the room, before reaching that form in which it is alone stable at such a temperature, it affords a striking illustration of Ostwald's "Gesetz der Umwaldlungstufen".⁵

4. *Sulphur From the Interaction of Normal and Polysulphides With Bromine and Iodine. (Preliminary Experiments.)*—The results obtained in paragraph 2. of this section showed that it would be impossible to obtain more than a few percent. of insoluble sulphur by treating polysulphides with acids, owing to the fact that if very concentrated acid was used, one obtained hydrogen polysulphides.

Since traces of iodine⁶ in heated sulphur increased the percentages of amorphous sulphur obtained, and it was known that in the preparation of hydriodic acid, by the reaction of iodine and hydrogen sulphide, sulphur

¹ Berthelot, *Ann. chim. phys.*, (3), 49, 430; Dammer "Handbuch," 4, 207.

² Tittinger, *Pharm. Post*, 27, 297.

³ Fritzsche, *Pogg. Ann.*, 42, 453.

⁴ This conclusion has already been stated by Peterson (*Z. physik. Chem.*, 8, 608) and by Muthmann. (*Z. Krystallographie*, 17, 342).

⁵ *Handbuch*, 2, 2, 444, 458.

⁶ Berthelot, *Compt. rend.*, 56, 39; Smith and Holmes, *This Journal*, 27, 999.

containing considerable proportions of the amorphous variety was formed, it was decided to try the actions of bromine and iodine, dissolved respectively in potassium bromide and potassium iodide, upon the normal and polysulphides of sodium.

The precipitated sulphur was filtered off and dried and extracted as described above. Some of the results of these preliminary investigations are given in the following table.

Source of sulphur	Precipitant	Percent. S _μ obtained
2.5 N Na ₂ S ₈	2.5 N I	8.0
2.5 N Na ₂ S ₈	2.5 N Br	24.0
2.5 N Na ₂ S ₈	2.5 N I	7.5
2.5 N Na ₂ S ₈	2.5 N Br	20.0

The sulphur precipitated by iodine came down quite soft, but not oily, and hardened much more quickly than the sulphur precipitated by bromine.

The reaction of bromine caused a considerable evolution of heat, so these results cannot be considered quantitative. It was decided to reserve this field for further investigations. (Section III of this paper.)

5. *Sulphur From the Interaction of Sodium Thiosulphate With Acids. (Preliminary Experiments.)*—In the following table are given the results of twelve experiments with different acids, and with different concentrations of the same acid. In all these preliminary experiments, save where the contrary is stated, the acid was simply poured into 100 cc. of the sodium thiosulphate solution.

	Conc. of Na ₂ S ₂ O ₃ (100 cc.)	Precipitant	S _μ
1	4N	50 cc. HCl, conc. (12N)	34.0
2	4N	100 cc. HCl, conc. (12N)	39.2
3	4N (saturated with KCl)	50 cc. HCl, conc. (12N)	19.5
4	4N	50 cc. HCl, 6N	6.5
5	8N	500 cc. HCl, conc. (12N)	95.0 ¹
6	(50 g. solid Na ₂ S ₂ O ₃ , 5H ₂ O)	100 cc. HCl, conc. (12N)	94.6 ²
7	4N	25 cc. HNO ₃ , conc. (16N)	56.5
8	4N	100 cc. HNO ₃ , 5N	15.7
9	4N	100 cc. H ₂ SO ₄ , conc.	20.2
10	4N	100 cc. H ₂ SO ₄ , 12N	21.3
11	4N	100 cc. acetic, glacial	0.0
12	4N	300 cc. " "	0.0

The above experiments show that,

(1.) Contrary to Berthelot's belief, the same sulphur compound may give sulphur wholly soluble (Exps. 11 and 12) or almost wholly insoluble (Exp. 5) in carbon disulphide, according to the precipitant used, and that different concentrations of the same precipitant may give different results (Exps. 1 and 4.)

(2.) Contrary to Cloez's belief, a solution which is not alkaline (Exps. 11 and 12), but strongly acid, may give wholly soluble sulphur.

¹ The solution of the thiosulphate was slowly added to the vigorously stirred acid.

² The finely powdered thiosulphate was slowly added to the vigorously stirred acid.

(3) An excess of the precipitating acid is not needed in order that appreciable amounts of insoluble sulphur may be found (Exps. 4 and 7.) That in these cases the 6.5 per cent. and the 56.5 per cent. of insoluble sulphur is not due to the free sulphurous acid liberated by the action, is shown by the negative result in Exp. 12, where much sulphur was liberated and therefore much free sulphurous acid was present.

(4) With sufficiently high concentrations of the acid, the thiosulphate being taken 8N to reduce the amount of water which it introduces into the system, and the solution of the salt being poured into the acid in order that there may be present at all stages of the precipitation the greatest possible concentration of the acid, a practically quantitative production of insoluble sulphur may be achieved.

(5) The concentration of the ionic hydrogen is a factor in the result, for, when the thiosulphate solution is saturated in advance with potassium chloride to repress the ionization of the acid, the percentage of S_{μ} falls from 34 (Exp. 1) to 19.5 (Exp. 3).

(6) It appears probable that the large thermal effect when sulphuric acid was used (Exps. 9 and 10) was responsible for the relatively small yield of S_{μ} . An amount of hydrochloric acid chemically equivalent to the amount of sulphuric acid gave almost twice as large a proportion of S_{μ} (Exps. 1 and 2).

6. *Effect of Temperature.*—In the above experiments no attention was given to the temperature which of course varied in consequence of thermal effects during the precipitation. It was self-evident however that temperature would exert considerable influence.

To learn more definitely the effects of temperature upon the result three experiments were made with solutions previously brought to 0°, 25° and 40°, respectively.

To secure known concentrations and otherwise similar conditions, equal volumes of 2N sodium thiosulphate and 10N hydrochloric acid were taken and were poured simultaneously and with equal speed into a third vessel.

Temperature	0°	25°	40° ¹
Per cent. of S_{μ}	47.1	34.0	30.8

II. Final Method of Precipitation.

Some of the preliminary experiments, particularly those in which the thiosulphate was added to the acid instead of the acid to the thiosulphate, had shown that, to secure easily formulated results, definite concentrations must be maintained throughout the process of mixing. This could be done only by arranging the two materials so that the quantities to be used were contained in equal volumes of liquid and then by running the two liquids at equal speed into a mixing vessel. It also had been shown

¹ Also see Section IV.

that definite temperatures would have to be chosen and maintained constant, in spite of thermal effects, during the mixing. When low concentrations were used the thermal effects were negligible and it was sufficient to pour the solutions, at the desired temperature, simultaneously into a vessel in which constant agitation was secured by means of a stirring apparatus. When more concentrated solutions were used the rate of flow of the liquids and the temperature were regulated by means of the apparatus shown in Fig. 2. Two accurate burettes of 50 cc. capacity, and having

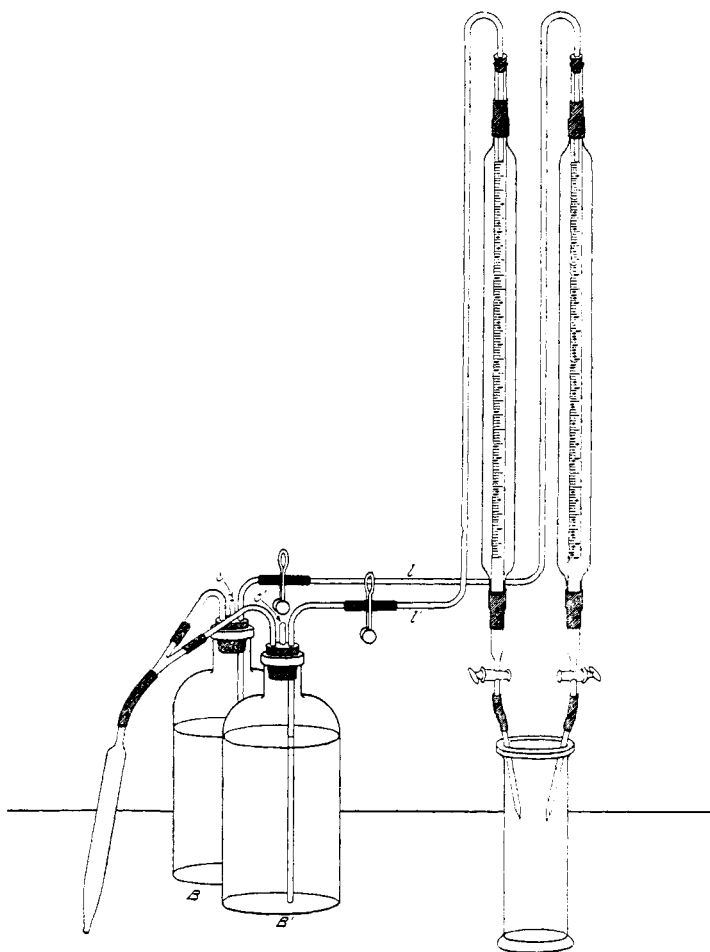


FIG. 2.

scale divisions of almost exactly the same length, were encased in the outer jackets of Liebig's condensers. The solutions contained in *B* and *B'* were forced, by means of compressed air, into the burettes through the tubes *L* and *L'*. When the pressure was released and *C* and *C'* were opened the

excess of each liquid flowed automatically back into B and B¹ and the burettes were left filled exactly to the zero marks. The liquids in B and B¹ were brought to a temperature close to that desired and water of the proper temperature flowing through the jackets completed the adjustment in this respect. Rapid and complete mixing was secured by the glass stirring apparatus. Complete duplicates were made of almost all the experiments and the data given are means of closely concordant results.

III. Percentages of S_μ in Sulphur Precipitated from Sulphides with Bromine and Iodine.

In these experiments the iodine and bromine were dissolved in aqueous solutions of potassium iodide and potassium bromide, respectively. Two different concentrations of the halogens, and two different concentrations each of sodium sulphide and sodium polysulphide were used. The table shows the concentrations before mixing. The temperature was 0°.

Concentration of Iodine:	Percentage of Amorphous Sulphur				
	2N Na ₂ S	2.5N Na ₂ S	5N Na ₂ S	2.5N Na ₄ S ₂	5N Na ₄ S ₂
2.5N.....		8.4	2.4	7.9	1.5
5.0N.....	36.5	43.5	20.3	18.5	15.5
Concentration of Bromine:					
2.5N.....		34.6	30.5	28.7	25.9
5.0N.....		(S ₂ Br ₂)	59.8	(S ₂ Br ₂ + S)	55.9

It will be noted that :

- (1) Bromine gives much larger proportions of S_μ than does iodine.
- (2) Excess of the halogen, although potent, is not essential to the formation of S_μ.
- (3) Equivalent amounts of iodine and the sulphide, both 2.5N, give 8.4 per cent. ; equivalent amounts, both 5N, give 20.3 per cent. ; two equivalents of iodine, *i. e.*, great excess, gives 43.5 per cent. Similar effect of change in concentration is shown by the polysulphide, and when bromine is substituted for iodine.
- (4) Excess of bromine gives sulphur bromide.

IV. Percentages of S_μ in Sulphur Precipitated from Thiosulphate with Acids.

Experiments With Hydrochloric Acid.—Many of these experiments were made at 0°, 25°, and at 40° in order to learn the effect of temperature. In the following tables the first column shows the concentration of hydrochloric acid before mixing; the second and third show the concentration of the acid and of the hydrogen ions (the latter very roughly), at the instant after mixing. The latter figures are calculated on the assumption that the acid is simply diluted with an equal volume of water. The columns following show the percentage of S_μ with various concentrations of sodium thiosulphate. The last column contains remarks on the state of the sulphur when first precipitated.

At 0°						
Conc. of HCl used	Conc. after mixing HCl	Hydrogen ions	Conc. 2N	Na ₂ S ₂ O ₃ and 4N	per cent. S _μ 6N	State of sulphur from 2N Na ₂ S ₂ O ₃
2N	1N	0.80	6.1	Yellow-brown, viscous, oil
3N	1.5N	1.10	12.4	14.7	8.3	" " " "
4N	2N	1.35	20.4	More viscous
5N	2.5N	1.55	21.5	18.9	29.6	" "
10N	5N	2.00	47.0	45.9	57.7	Very viscous
12N	6N	2.10	68.8	72.3	75.9	" "

At 25°							
Conc. HCl used	Conc. after mixing HCl	Hydrogen ions	2N	Conc. Na ₂ S ₂ O ₃ and 4N	per cent. S _μ 6N	8N	State of Sulphur from 2N Na ₂ S ₂ O ₃
2N	1 N	0.80	6.4	..	3.2	..	Yellow-brown, viscous, oil
3N	1.5N	1.10	12.9	7.9	7.0	6.6	" " " "
4N	2 N	1.35	13.6	15.9	22.0	25.1	" " " "
5N	2.5N	1.55	22.5	19.1	28.5	39.2	More viscous
10N	5 N	2.00	33.6	52.0	55.9	62.2	Very viscous
12N	6 N	2.10	45.0	67.6	72.4	79.3	" "
*	10 N	1.70	85.6	Non-viscous powder

* This result obtained by mixing 50 cc. of 6N Na₂S₂O₃ with 250 cc. of 12N HCl.

At 40°

Conc. HCl used	Conc. after mixing HCl	Hydrogen ions	per cent. S _μ 2N Na ₂ S ₂ O ₃	State of Sulphur
2N	1 N	0.80	5.5	Yellow-brown, viscous, oil
3N	1.5N	1.10	6.8	" " " "
4N	2 N	1.35	11.9	" " " "
5N	2.5N	1.55	18.5	More viscous
10N	5 N	2.00	30.8	" "
12N	6 N	2.10	34.2	Very viscous

It will be noted that:

(1) The percentages of S_μ is not proportional to the excess of acid, for when there is only an equivalent amount of the latter large quantities of S_μ were obtained, and even when there was excess of the thiosulphate quantities of S_μ up to nearly 40 per cent. were formed. That the S_μ is not due to the sulphurous acid liberated, was shown by the preliminary experiments.

(2) That in a given concentration of the thiosulphate, the percentages of S_μ are directly proportional to the concentrations of the acid after mixing is shown by the straight lines obtained by representing some of the results graphically in Figs. 3 and 5. The abscissae show the percentages of S_μ and the ordinates the concentrations of the acid.

(3) Since the preliminary experiments had indicated a diminution of the S_μ when the ionization of the acid was repressed by means of potassium chloride, the concentration of the hydrogen ion after mixing has also been plotted (Figs. 4 and 6) against the percentages of S_μ¹. The curves

¹ In view of the work by Oettingen, Z. physik. Chem., 33, 1, upon "The Reaction of Sodium Thiosulphate with Acids," these results seem to show that the percentages of S_μ precipitated from sodium thiosulphate by means of acids may be proportional to the velocity of the precipitation and consequently proportional to the size of the particles precipitated. Consideration of Section V, however, proves any such relationship to be purely incidental.

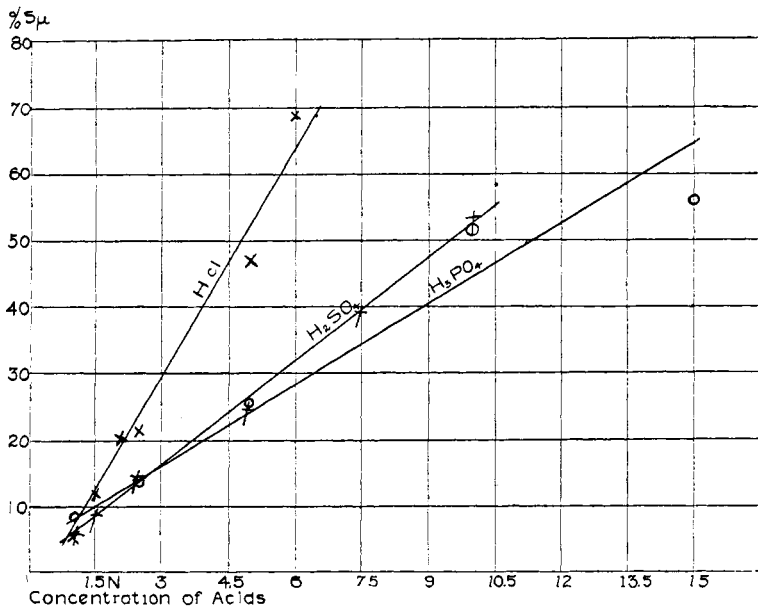


FIG. 3. Twice Normal Sodium Thiosulphate and Acids. 0°

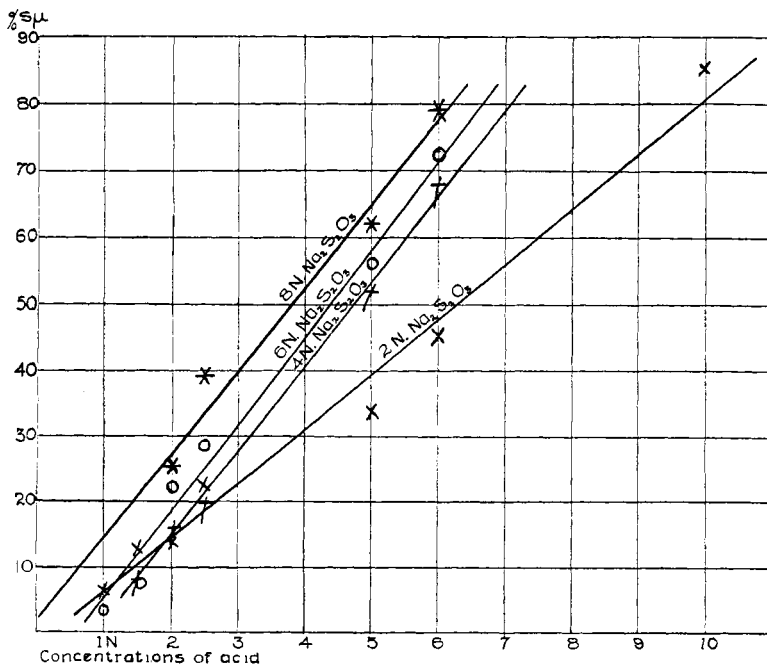


FIG. 5. Sodium Thiosulphate and Hydrochloric Acid. 25°

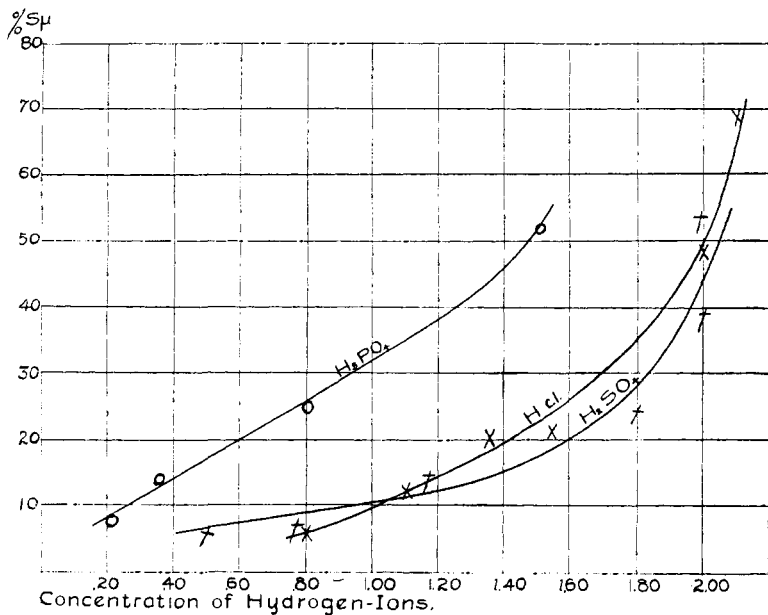


FIG. 4. Twice Normal Sodium Thiosulphate and Acids. 15°.

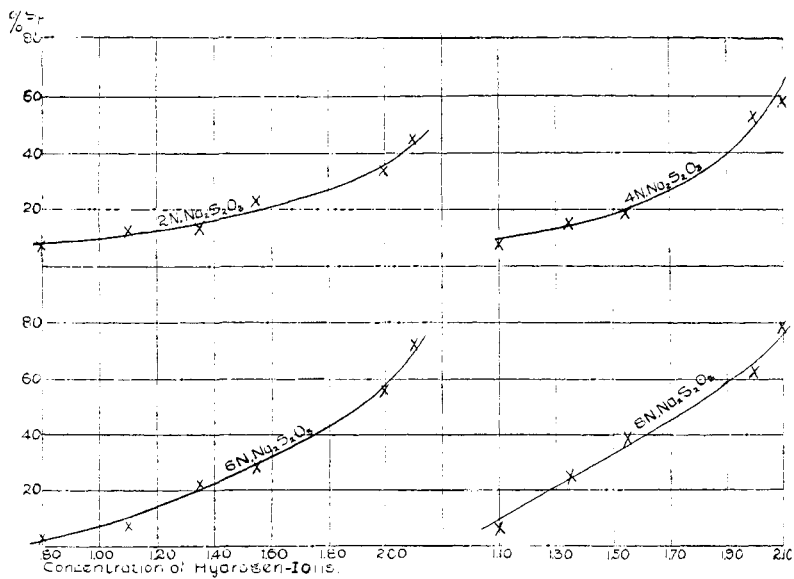


FIG. 6. Sodium Thiosulphate and Hydrochloric Acid. 25°.

indicate that the percentages of S_u increase more rapidly than the concentrations of the hydrogen ion.

That the concentration of the hydrogen ion is only one factor is shown

in several ways. For example, at 25°, when the concentration of the acid was very great, and that of the hydrogen ion therefore less than at lower concentrations, the percentage of S_μ was nevertheless the greatest of all (see experiments with phosphoric acid).

(4) When corresponding results at different temperatures are compared, it will be seen that the proportions of S_μ are in general smaller the higher the temperature. This corresponds with the fact that S_μ when once hardened is more permanent at lower temperatures.

Experiments With Sulphuric and Phosphoric Acids.—The data in the following table are stated in the same way as for hydrochloric acid. The temperature was 0°.

Conc. of acid used	At 0°					
	Sulphuric acid		Percent. S _μ 2N Na ₂ S ₂ O ₃	Phosphoric acid		
	Conc. after mixing H ₂ SO ₄	Hydrogen ions		Conc. after mixing H ₃ PO ₄	Hydrogen ions	
2N	1 N	0.50	6.5	1 N	0.21	S.1
3N	1.5N	0.76	8.7
5N	2.5N	1.16	14.4	2.5N	0.36	14.0
10N	5 N	1.80	24.4	5 N	0.80	25.0
15N	7.5N	2.00	38.7
20N	10 N	1.99	53.0	10 N	1.46	52.4
30N	15 N	..	55.9

It will be noted that :

(1) For the observations with sulphuric acid, and for those with phosphoric acid excepting the last of the series, the percentages of S_μ are closely proportional to the concentration of the acid.

(2) Although 2N sulphuric acid gives about the same proportion of S_μ as does 2N hydrochloric acid (6.5 and 6.0 percent. respectively), yet the proportion does not afterwards rise nearly so rapidly with increasing concentrations of the former acid.

(3) Comparing the effects of mixtures isotonic in respect to hydrogen ions we find that the results with sulphuric acid are not very regular. Phosphoric acid gives, however, unexpectedly large proportions of S_μ, approximately twice as great as those given by hydrochloric acid. The highest concentration of sulphuric acid, like the highest hydrochloric acid, although furnishing a relatively small concentration of hydrogen ions, gives by far the greatest percentage of S_μ.

V. By which Conditions and at what Stage is the Percentage of S_μ Determined?

The work in the preceding sections having shown that fairly constant results could be obtained with constant conditions, the next problem was to ascertain which of these conditions determined the proportion of S_μ ultimately found. In particular, is the proportion of S_μ determined by the proportion of the interacting substances and at the

instant of liberation, or is it determined by a contact action of the resulting liquid mixture upon the sulphur, and during the process of hardening? An answer to these questions was sought by separating the sulphur, within a few moments after the precipitation from the original liquid and substituting for this during the period of hardening, either pure water, more concentrated hydrochloric acid than that used in precipitating, or ammonium hydroxide solution.

Results of Contact Experiments.—Specimens of precipitated sulphur which tended to remain fluid for a considerable length of time were required and the most favorable material for the purpose is that formed by mixing equal volumes of 2N sodium thiosulphate with 2N or 3N hydrochloric acid. The sulphur was precipitated as in Section II, and the liquid was immediately poured off. The acid, water or ammonia was then quickly poured into the sulphur and the materials were violently stirred together. For the purpose of comparison, experiments were made under identical conditions, in which, however, the specimen of sulphur remained in contact with the original liquid.

Conc. HCl with 2 N Na ₂ S ₂ O ₃	Original Liquid		Sulphur in contact with 6N HCl		2N HCl	
	Time	Percent. S	Time	Percent. S	Time	Percent. S _μ
2N	1 day	5.0	1 day	24.1	2.5 hrs.	45.1
	10 days	6.0	1 day	36.2	2.5 hrs.	47.8
					10 days	53.4
3N	10 days	11.8			10 days	65.6
	10 days	12.4			10 days	51.7

Sulphur precipitated with 2N HCl and left for 10 days in contact with pure water gave 0.6 per cent. S_μ. The same, left in contact with ammonium hydroxide for 10 minutes or 5 minutes, and then washed, gave 0.2 and 0.3 per cent. S, respectively.

It will be observed that where the sulphur remained in contact with the original liquid, the duplicate results are concordant, and agree closely with those obtained at 0° in Section IV. The lack of concordance in the duplicate experiments in which stronger acid was mixed with the sulphur are due to the unavoidable absence of constancy in the process of mixing.

It was observed that in every case where water or an acid was allowed to remain in contact with the liquid sulphur a considerable amount of hydrogen sulphide was formed, a fact which shows the decided chemical activity of this less stable form of sulphur.

The immediate conclusions from these experiments are:

(1) That contact with strong hydrochloric acid increases the yield of S_μ, and that the amounts produced are of the same order as those obtainable when the stronger acid is used for the original precipitation (see Section IV).

(2) That a very brief contact produces almost as great an effect as prolonged contact.

(3). That when ammonium hydroxide is used, the oily sulphur instantly crystallizes and retains only a trace of S_{μ} .

(4) Taking into consideration previous experiments we conclude that the percentage of S_{μ} is jointly determined by the nature and concentration of the precipitants, and by the nature and concentration of the materials remaining in contact with the sulphur.

The Theory of Sulphur Precipitation.—The increase in the yield of S_{μ} resulting from contact of the oily sulphur with strong hydrochloric acid, during hardening might be explained in two ways.

The oily sulphur may originally contain more S_{μ} than the largest proportion of amorphous sulphur obtainable from it, and contact with stronger acid must then reduce the speed with which reversion to S_{λ} takes place and permit the survival of the larger percentage of S_{μ} . On the other hand, the stronger acid may really increase the yield of amorphous sulphur by converting S_{λ} into S_{μ} .

The latter supposition is supported by Berthelot's¹ statement that soluble sulphur becomes in part soluble when allowed to stand in acid liquids. But Smith and Holmes² repeated Berthelot's work with an improved method of analysis, and were unable to discover any such effect. It was easily conceivable, however, that while the relatively coarse grained sulphur obtained by pulverization was unaffected, the very finely divided sulphur produced by precipitation might be changed to a marked extent. The soluble sulphur precipitated from sulphides, after solidification, was therefore allowed by us to stand for periods up to thirty days in concentrated (12N) hydrochloric acid and in 6N sulphuric acid. In no case, however, was even a trace of insoluble sulphur produced by this treatment. Nitric acid oxidized this finely divided sulphur so rapidly that it was not used. We believe, therefore, that soluble sulphur, *after it has once solidified*, is not changed into insoluble sulphur to the slightest extent by these substances.

That this solid S_{λ} , or even the droplets of soluble sulphur before solidification, can be so changed seems theoretically very improbable. In the equilibrium $S_{\lambda} \rightleftharpoons S_{\mu}$, the proportion of S_{μ} at 20° is practically zero. A catalytic agent, (contact agent) would only bring the proportion nearer to that proper to the equilibrium, and would not increase the amount of S_{μ} . If hydrochloric acid actually operated so as to increase the amount of S_{μ} it could do so only by playing the rôle of a regular component of the system. That iodine does play such a rôle and does displace this equilibrium in molten sulphur has been shown by Smith and Carson³, but the displacement is small at the lower temperatures. Here we have

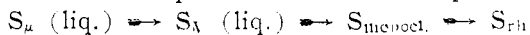
¹ Ann. chim. phys. (3) 498, 442.

² This Journal, 27, 1003, or Z. physik. Chem., 54, 282.

³ Z. physik. Chem., 57, 692.

to account for an apparent raising of the proportion of S_{μ} from zero to values often over 50 per cent., and in one case to 96 per cent. The alternative explanation, that much S_{λ} is contained in the freshly precipitated fluid sulphur and that contact with concentrated hydrochloric acid retards the reversion to S_{λ} and enables more S_{μ} to be secured, is theoretically more plausible and can be shown also to accord better with the facts.

The explanation which seems most probable may be stated thus:—In accordance with the principle of "Umwandlungsstufen," the sulphur at the moment of liberation is all in the least stable form, namely that of S_{μ} . In pure water, or in an alkaline liquid, the droplets, (or the fluid, if the droplets flow together) then pass successively through the stages fluid S_{μ} , fluid S_{λ} , solid monoclinic sulphur, solid rhombic sulphur:



When a retarding catalyser such as hydrochloric acid is present in excess, or is quickly mixed with the S_{μ} , the change to S_{λ} is retarded and much of the S_{μ} hardens to amorphous sulphur (super-cooled S_{μ}). That even with equivalent amounts of sodium thiosulphate and hydrochloric acid about 5 per cent. of S_{μ} survives, while with sodium polysulphide and the same acid or sodium thiosulphate and acetic acid in equivalent amounts none is obtained, seems to show that the nature of the interaction plays a part, although a subordinate part, in the result.

That in molten sulphur the rate of reversion of S_{μ} to S_{λ} may be markedly diminished by hydrogen chloride, phosphoric acid and sulphur dioxide, and the survival of S_{μ} in the amorphous form made possible was shown by Smith and Holmes¹. Contrariwise, the accelerating effect of ammonia was noted by the same observers. These effects were studied in greater detail by Smith and Carson². It is justifiable, therefore to attribute the survival of S_{μ} and the production of amorphous sulphur in precipitation to the same cause as has already been shown to operate in the chilling of strongly heated, molten sulphur. The assumption that the precipitated sulphur is at first wholly S_{μ} is justified by the theory, and by the fact that in one experiment (Section I, 4) as much as 96 per cent. was actually isolated as amorphous sulphur. The contact actions of differing concentrations of hydrochloric acid (or of iodine in Section III) determine the degree of retardation of the change to S_{λ} and therefore the proportions in which soluble, rhombic sulphur, and insoluble, hardened S_{μ} enter into the final product of precipitation. The intermediate formation of monoclinic sulphur (or perhaps one of the other unstable, crystalline forms) suggested in the scheme is supported by the polariscopic observations described in Section I, 3.

Supplementary Experiments.—It was thought that confirmation of the

¹ *Ibid.*, 57, 688.

² *Z. physik. chem.*, 57, 692.

above view might be obtained by taking the freshly precipitated oily sulphur and chilling it with liquid air. Two specimens were placed in liquid air for $2\frac{1}{2}$ hours. Both became at once perfectly hard. One was ground repeatedly in a mortar under liquid during this time. When allowed to become warm again, however, both specimens returned to the oily condition, and, being now free from acid, eventually gave almost pure soluble sulphur (amorphous sulphur 0.3 and 1.8 per cent, respectively). Apparently, therefore, the hardening which marks the transition from liquid S_{μ} to amorphous sulphur cannot be hastened by cooling, so that proof that the oil is S_{μ} was not obtainable in this way.

Another interesting question presented itself. This was whether, in a sample yielding a medium per cent. of amorphous sulphur, during the change of the S_{μ} to S_{λ} on the one hand and to hardened, amorphous sulphur on the other. The phenomenon consists in a complete change of certain droplets of S_{μ} (as wholes) into S_{λ} and of certain others into amorphous sulphur, or whether each droplet solidifies to a mass made up of a certain percentage of each. We attempted to repeat the polariscope observations described in Section I, 3, using, however, a suspension of precipitated sulphur, which should have given a considerable proportion of amorphous sulphur, instead of one giving only pure soluble sulphur. We have again to thank Prof. Iddings for cooperating with us in these experiments. The droplets were examined just after precipitation, and again after standing for 10 days, to determine whether each particle contained some amorphous sulphur, or whether some consisted wholly of this form and others contained none. The hardened material was also treated with carbon disulphide under the polariscope, to determine whether some particles were wholly soluble, and others insoluble, or whether parts of every one were attacked. Unfortunately, the droplets obtained under conditions which give amorphous sulphur are so small that no definite conclusion could be reached with instruments which showed the effects already described with perfect clearness.

Summary of Results.

1. Berthelot's and Cloez's rules do not give a correct formulation of the facts, inasmuch as polysulphides do yield S_{μ} when treated with concentrated active acids, but with dilute acids yield no S_{μ} .

2. The so-called "soluble" or "soft" "amorphous sulphur" formed by precipitation from polysulphides is not amorphous but is actually crystalline sulphur.

3. There has been devised a method of precipitating sulphur, with concentrations and temperature remaining constant during the precipitation, and this method gives constant results.

4. The proportions of S_{μ} formed when iodine and bromine interact with sulphides and polysulphides have been studied quantitatively.

5. The proportions of S_m when acids, such as acetic, phosphoric, sulphuric and hydrochloric interact with sodium thiosulphate have been studied quantitatively.

6. With acetic acid and the thiosulphate no S_m is produced, with the other acids the percentages of S_m is in each case proportional to the concentrations of the total acid in the mixture at the moment of precipitation.

7. The concentration of ionic hydrogen seems to be a factor in determining the proportions of S_m , but it is evident that they determine it jointly with other factors which have not yet been determined.

8. It has been shown that the proportion of amorphous sulphur produced by precipitation is determined in part by the nature of the interacting materials, but that a contact effect of the whole liquid in which the liberated sulphur is suspended exercises a still greater effect. The conclusion is that the freshly liberated sulphur is initially all S_m , and that the reversion to S_λ is retarded during the hardening by the contact action of the acid or halogen in the liquid, different concentrations of the contact agent permitting differing proportions of S_m to overcome the tendency to revert and thus to remain finally as amorphous sulphur. In conclusion, I desire to thank Professor Alexander Smith for all of his kindly assistance during the progress of this investigation.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS].

SOME NEW FORMS OF APPARATUS.

BY WILLIAM M. DEHN.

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When a drop of pure mercury is placed in a clean tube whose internal diameter is less than 3 mm. the metal assumes and retains a cylindrical form owing to the tension exerted by the mercury surfaces not in contact with the glass. The cylinder of mercury may then act as an air tight piston, possessing very easy mobility¹. A difference of gas pressure on the two ends of the cylinder results in a movement of the mercury until equilibrium is established, the slight friction of the mercury on the glass and the inertia of the mercury being readily overcome by gentle tapping at the end of the tube or on the glass above the mercury drop. Some of the following experiments have shown that this drop of mercury is sensitive to a difference of pressure less than 0.1 mm.

Hygrometer.—The apparatus is constructed as follows:—The bulb C made from a small flask (20-50 cc.) is attached first to the stopcock B and then to the side-tube D. This side-tube is made from a 1 cc. pipette graduated to 0.01 cc. and must have an internal diameter less than 3 mm. The apparatus without A attached is weighed empty and is then filled with

¹ Z. physik. Chem. 11, 587.