[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OREGON AGRICULTURAL EXPERIMENT STATION.]

THE REACTION BETWEEN SULFUR AND CALCIUM HYDROXIDE IN AQUEOUS SOLUTION.

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Introduction.

In a previous paper[1] reference was made to the commercial use of the reaction between calcium hydroxide and sulfur in the manufacture of the "lime-sulfur" spray, an insecticide now in wide general use. At that time, a résumé was also given of the literature on this and the analogous reactions of the alkali metals.

The particular difficulty which presented itself in the study of the reaction between sulfur and calcium hydroxide was the easy decomposition of the calcium thiosulfate formed, into calcium sulfite and free sulfur. This decomposition obscures the primary reaction which takes place. Experiments, similar to those used in previous work,[1] were tried and it was found practically impossible to combine even small amounts of calcium hydroxide and sulfur in heated aqueous solutions without some decomposition of the thiosulfate produced. This decomposition occurs at temperatures much below 100°. After some more or less unsuccessful work had been done along this line, it was decided to attack the problem from a different standpoint. This will be explained in what follows.

Experimental.

The analytical methods employed were the same as used in former work.[2] The meaning of the coined terms, "sulfide" sulfur and "polysulfide" sulfur used here, in discussing the kinds of polysulfides, is the same as that given in an earlier paper.[3] It is unnecessary to repeat the explanation at this time.

The sulfur used was purified by recrystallization from pure carbon disulfide in such a manner that a fine crystal-meal was obtained. This was pressed free from the mother liquor and thoroughly dried at a gentle heat. It was finely ground in a mortar and sifted through an 80-mesh sieve just before using. The calcium oxide used in making the hydroxide was prepared by heating a sample of "J. T. Baker's Analyzed, C. P." calcium carbonate in a muffle furnace until it was completely converted into the oxide. The distilled water had been recently boiled to expel oxygen and carbon dioxide.

Two different solutions, each containing mixtures of calcium tetrasulfide, pentasulfide, and thiosulfate in different amounts, were prepared by boiling

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[1] THIS JOURNAL, **35**, 1741 (1913).

[2] *Jour. Ind. Eng. Chem.*, **2**, 27 (1910); THIS JOURNAL, **35**, 1741 (1913).

[3] *Jour. Ind. Eng. Chem.*, **2**, 27 (1910).

calcium hydroxide and sulfur in water. In each case, the sulfur was used in slight excess and the boiling continued for more than an hour. For convenience, these solutions are designated as solutions A and B. The analyses of a 20 cc. aliquot portion of solution A and a 25 cc. aliquot portion of solution B, are given in Table I.

TABLE I.—COMPOSITION OF ALIQUOTS OF SOLUTIONS MADE BY BOILING CALCIUM HYDROXIDE AND SULFUR IN WATER.

Sample.	"Sulfide" sulfur, g.	"Polysulfide" sulfur, g.	Thiosulfate sulfur, g.	Total calcium, g. (Calculated as CaO.)	Free calcium hydroxide, g.	Sulfur combined as sulfite and sulfate, g.
20 cc. aliquot sol. A..	1.256	4.714	0.360	2.56	none	none
25 cc. aliquot sol. B..	0.866	3.178	0.936	2.42	none	none

A 20 cc. aliquot part of solution A was transferred to a liter volumetric flask containing 800 cc. of an almost saturated solution of calcium hydroxide. The flask was then connected to a hydrogen generator and pure hydrogen passed in until all the air had been expelled, in order to prevent any oxidation of the polysulfide to thiosulfate. After the removal of the air, the body of the flask was almost wholly immersed in water which was maintained at a temperature near 70°. The flask was kept in the water at this temperature for over two hours. During this time, it was gently shaken twice and a continuous stream of hydrogen passed in. Finally, the solution was allowed to cool, made up to 1000 cc. volume, and analyzed. For results see Expt. 1, Table II.

A second experiment, which was simply a duplicate of Experiment 1, was carried out. The results are also given in Table II.

In the third experiment a 25 cc. aliquot part of solution B was transferred to a half-liter volumetric flask containing 450 cc. of an almost saturated solution of calcium hydroxide. The flask was then handled in exactly the same manner as in Expt. 1, and the solution finally made to 500 cc. volume. The analytical data are given in Table II.

A duplicate of Experiment 3 was performed and the results obtained are given as Expt. 4 in the following table:

TABLE II.—COMPOSITION OF ALIQUOTS CONTAINING MIXTURES OF CALCIUM TETRASULFIDE AND PENTASULFIDE AFTER BEING HEATED IN SOLUTIONS CONTAINING EXCESS OF CALCIUM HYDROXIDE.

	"Sulfide" sulfur, g.	"Polysulfide" sulfur, g.	Thiosulfate sulfur, g.	Sulfate and sulfite sulfur, g.	Free calcium hydroxide, g.
Expt. 1..........	1.456	4.312	0.520	none	present in excess
Expt. 2..........	1.467	4.286	0.510	none	present in excess
Expt. 3..........	0.977	2.960	1.030	none	present in excess
Expt. 4..........	0.981	2.919	1.025	none	present in excess

A fifth experiment was made in the following manner: Exactly 41.38 g. of calcium hydroxide (prepared by slaking 31.32 g. of calcium oxide with water) were placed in a Jena glass flask, 2 liters capacity. To this were added 59.4 g. of sulfur, which had been thoroughly wetted, and enough distilled water to make the volume somewhat greater than 500 cc. The flask was then connected to a hydrogen generator as in the preceding experiments. The mixture of calcium hydroxide, sulfur and water was then heated to boiling and let boil briskly for 40 minutes, when the combination of the calcium hydroxide and sulfur seemed to be complete. During this time the flask was frequently shaken and a continuous stream of hydrogen passed in. The flask was next disconnected and the hot solution obtained was filtered quickly through a glass wool plug into a liter volumetric flask, cooled, made up to volume and analyzed. The results are given in Table III.

A duplicate of the preceding experiment was made and the results are recorded in Table III as Expt. 6.

Table III.—Composition of Solutions Obtained by Boiling Calcium Hydroxide and Sulfur in Water.

	"Sulfide" sulfur, g.	"Polysulfide" sulfur, g.	Thiosulfate sulfur, g.	Total calcium, g. (Calculated as CaO.)	Free calcium hydroxide, g.
Expt. 5........	11.52	35.56	11.50	30.15	none
Expt. 6........	11.55	35.41	11.49	30.27	none

Discussion of Results.

It will be noted that in the two solutions whose composition is given in Table I, the "polysulfide" sulfur is more than three times greater than that of the "sulfide" sulfur. If the polysulfide present were simply the tetrasulfide (CaS_4) it would be exactly three times greater. Evidently, the solutions both contain a mixture of calcium tetrasulfide and pentasulfide (CaS_5).

The data given in Table II show that the "polysulfide" sulfur is, considering the experimental error of analysis, three times greater than the "sulfide" sulfur, indicating that the polysulfide present is the tetrasulfide. Since there was an excess of calcium hydroxide in each of these solutions, *it is evident that calcium tetrasulfide is the lowest polysulfide formed when calcium hydroxide and sulfur react in aqueous solution.*

Comparing the results given in Tables I and II, it will be seen that in Table II there has been an increase in the amounts of both the "sulfide" sulfur and the sulfur combined as thiosulfate. In each of the experiments, these forms of combined sulfur increased in equal amounts. The data presented show that the *"polysulfide" sulfur in the aliquot parts from solutions A and B, which was in excess of that required to form the tetrasulfide of the calcium combined as polysulfide, has reacted in Experiments 1, 2, 3 and 4 with more calcium hydroxide.* The results from the experiments just enumerated also show that the primary reaction between calcium hydroxide and sulfur takes place as represented by the following equation:

$$3Ca(OH)_2 + 10S \longrightarrow 2CaS_4 + CaS_2O_3 + 3H_2O$$

This reaction is analogous to that occurring with potassium hydroxide and sulfur[1] except that with the potassium hydroxide the trisulfide (K_2S_3) is formed.

In Experiments 5 and 6 the calcium hydroxide and sulfur were used in amounts proportionate to those required in the equation given in the preceding paragraph. The analytical results show that there was but a slight loss of calcium and sulfur due to the formation of the more insoluble calcium sulfite. Since there was no uncombined calcium hydroxide present, all of this substance had reacted with the sulfur. This fact and the general relationships of the amounts of the different forms of combined sulfur with each other, confirm the conclusions drawn from the preceding experiments.

In solutions A and B where an excess of sulfur was used in preparation, some calcium pentasulfide was present. This justifies the conclusion that a secondary reaction took place in which sulfur combined with the tetrasulfide to form pentasulfide.

In conclusion, it may be well to state that a discussion of the commercial application of the results here reported, will soon be presented for publication in the *Journal of Industrial and Engineering Chemistry.*

Summary.

1. The primary reaction between calcium hydroxide and sulfur in heated aqueous solution takes place as represented by the following equation:

$$3Ca(OH)_2 + 10S \longrightarrow 2CaS_4 + CaS_2O_3 + 3H_2O$$

2. When sulfur is used in excess, a secondary reaction occurs in which it combines with the tetrasulfide to form pentasulfide.

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SOME PHYSICAL PROPERTIES AND THE ANALYSIS OF TERNARY MIXTURES OF TOLUENE, CARBON TETRACHLORIDE AND ETHYLENE BROMIDE.

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The literature of ternary systems appears to contain only two[2] cases in which unknown ternary mixtures of organic substances have been

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[1] *Loc. cit.*

[2] After this communication had been sent to the editor my attention was called to a case in which the composition of certain ternary mixtures was ascertained by determining their physical properties. Shinkichi Horiba has, namely, analyzed mixtures of water, ethyl alcohol, and ethyl ether by determining their specific gravities, indices of refraction, and specific viscosities. The original paper was published in the *Memoirs, Imperial University, Kyoto,* 3, 3, p. 63, (1911), and a brief abstract of it in the