

been shown that, *in a metal, the current is carried by negatively charged carriers.*

There has been much uncertainty among physicists as to the source of the negative carriers in metals. The results obtained in the study of radioactive substances have shown that atoms are very complex systems containing a considerable number of electrons. It has not always been clear as to what electrons in the atom are concerned in the conduction process. As a result of the study of electropositive groups, it is clear that it is necessary to distinguish between two classes of electrons in metals. There are certain electrons which enter into the internal structure of the atom itself. These are practically fixed in their orbital relations, and, possessing enormous energy, they are entirely unaffected by any change in the conditions to which we are at the present time able to subject them. On the other hand, in metals there are also present electrons which are held but loosely, which are in fact able to move freely from atom to atom. These electrons are very sensitive to changes in condition such as temperature, pressure, the presence of other atoms, etc. So weak is the bond uniting the electron to an atom that more electronegative atoms may remove it entirely from the original atom in question. *The electrons to which conduction is due in metals are the same electrons which are involved in the common chemical combination of metals with other elements.*

In chemical combinations the electronegative constituent takes up an additional negative electron for which the positive constituent has but a very small attraction. The less tendency the metal has to retain its electron, the more electropositive it becomes and the more readily does it, in general, react. Ordinarily, the positive and negative constituent of a compound are held together through the medium of the electrons. Under certain conditions, however, (for example in solution in a dielectric medium) the electrostatic force acting between the metallic atom and its electron becomes weakened to such an extent that the negative constituent escapes carrying the electron with it. The same result may be obtained at high temperatures with the fused salt or even with the solid compound.

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

## ON THE REACTION BETWEEN SULFUR AND POTASSIUM HYDROXIDE IN AQUEOUS SOLUTION.

By HERMAN V. TARTAR.  
Received August 11, 1913.

### Introduction.

In connection with some investigations on the "lime-sulfur" spray, now so widely used as an insecticide, the author had occasion to look up

the literature relating to the reactions of the alkali and alkaline earth hydroxides with sulfur. It was found that all the work which had been done by the various investigators was imperfect, because of the faulty methods used for the examination of the solutions containing the products of the reactions. In fact, the study of the literature showed that the *primary* reaction of sulfur with any of the alkali or alkaline earth hydroxides has never been determined.

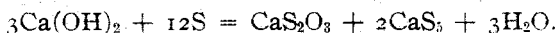
While making an investigation of the chemical composition of the "lime-sulfur" spray,<sup>1</sup> methods were developed in this laboratory which might also be used in studying the reaction between sulfur and any of the hydroxides mentioned. And because of the large commercial use of the reaction between calcium hydroxide and sulfur in the manufacture of spray material ("lime-sulfur" spray) a study of this reaction was considered. A serious difficulty which presented itself, however, was the easy decomposition of calcium thiosulfate, one of the products of the reaction, into calcium sulfite and sulfur in heated aqueous solutions. After some more or less unsuccessful work had been done, it was deemed advisable to first make a study of the reaction of sulfur with one of the alkali hydroxides (where there would be no decomposition of the products of the reaction), before proceeding further with the study of the reaction of sulfur with calcium hydroxide. With this idea in mind, the study of the reaction of sulfur with potassium hydroxide was undertaken.

#### Historical.

Fordhos and Gélis<sup>2</sup> concluded that, when sulfur is heated with a solution of potassium hydroxide, thiosulfate and polysulfide are formed. The results obtained indicated that the amounts of the different substances formed varies under different conditions.

Fahlberg and Iles<sup>3</sup> reported that when sulfur is melted with potassium hydroxide under certain conditions, polysulfide and thiosulfate are formed. When an excess of the alkali is present only sulfite and sulfate are produced.

In 1884, Divers and Shimidzu<sup>4</sup> found that calcium pentasulfide and thiosulfate are formed when calcium hydroxide and sulfur are boiled together in water. Later, Divers<sup>5</sup> states that "at first the pentasulfide may be largely in excess of the thiosulfate, although it is not known to have been in such excess as the following equation requires:



<sup>1</sup> *J. Ind. Eng. Chem.*, 2, 271 (1910).

<sup>2</sup> *Ann. chim. phys.*, [3] 18, 86 (1846).

<sup>3</sup> *Ber.*, 11, 1187 (1878).

<sup>4</sup> *J. Chem. Soc.*, 45, 270 (1884).

<sup>5</sup> *Ibid.*, 696 (1884).

Senderens<sup>1</sup> studied the reactions of the oxides of the alkali and alkaline earth metals when boiled with sulfur and water. His results indicated that they react as represented by the following general equation:



He also found that with dilute solutions a greater amount of thiosulfate was formed from the decomposition of the polysulfide.

Pomeranz<sup>2</sup> supposed that the primary reaction between the alkali hydroxides and sulfur is analogous to that between the alkali hydroxides and chlorine in the cold, and takes place as represented in one of the following equations:



or



In support of this view, Pomeranz states that a mixture of sulfur and sodium hydroxide in the ratio  $2S : 3NaOH$  has a similar bleaching action on *p*-nitroaniline-red to that of sodium hyposulfite. He holds that the polysulfide and thiosulfate are only produced by the further reaction of sulfur on the sulfide and hyposulfite.

The work of Haywood,<sup>3</sup> Thatcher,<sup>4</sup> and Bradley and the author<sup>5</sup> show that the products formed by the reaction of sulfur with calcium hydroxide in heated aqueous solutions are calcium polysulfide and thiosulfate. Thatcher concluded from his incomplete data that the reaction in dilute solution might take place as indicated by the following equation:



The author and Bradley showed that in solutions resulting from this reaction both calcium tetrasulfide and pentasulfide were present.

On the whole, the literature shows that the products formed by the reaction of sulfur with the alkali and alkaline earth hydroxides are polysulfides and thiosulfates. In practically all of the investigations, air was not excluded from contact with the products of the reaction. The neglect of this precaution introduced an error due to the rapid oxidation of the polysulfides. Again, most of the experiments were made using an excess of sulfur and, evidently, without thought of a possible secondary reaction of sulfur with the products formed by a primary reaction. Lastly, previous work has been handicapped because no methods have been available for determining the amount of the hydroxide of a metal present in solutions also containing polysulfides and thiosulfate of the same metal.

<sup>1</sup> *Bull. soc. chim.*, [3] 6, 800 (1891).

<sup>2</sup> *Z. Farb. Text. Ind.*, 4, 392 (1905).

<sup>3</sup> THIS JOURNAL, 27, 244 (1905).

<sup>4</sup> *Ibid.*, 63 (1908).

<sup>5</sup> *Loc. cit.*

### Methods of Analyses.

For the study of this reaction, methods for the determination of sulfur present in the form of polysulfides, of thiosulfate, of sulfite, and sulfate are required; also of potassium combined as polysulfides, as thiosulfate, and as hydroxide.

The potassium in the form of thiosulfate and sulfur present as polysulfide, as thiosulfate, and as sulfite and sulfate were determined according to the methods outlined by Haywood.<sup>1</sup>

For the determination of potassium combined as polysulfides, a well-known analytical method<sup>2</sup> has been slightly modified. As it is used here, the zinc is not precipitated as the monosulfide, but as the polysulfide. It has been found that when an ammoniacal solution of zinc chloride is added to a solution of a potassium polysulfide, the corresponding polysulfide of zinc is formed; *e. g.*, from a solution of potassium trisulfide zinc trisulfide is formed, and from potassium tetrasulfide, zinc tetrasulfide. In the determination, the titration with the tenth-normal zinc chloride solution was carried out as in the method for "sulfide" sulfur, reported in former work.<sup>3</sup> The number of cubic centimeters of the solution required is the tenth-normal titration of the potassium combined as polysulfide.

Potassium hydroxide was estimated by the method used for the determination of calcium hydroxide in the "lime-sulfur" spray.<sup>3</sup>

### Experimental.

The sulfur used was purified by recrystallization from pure carbon disulfide in such a way 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 just before it was used. A sample of "J. T. Baker's Analyzed" potassium hydroxide (by alcohol) was employed. This material was quite pure, containing but 0.08% of carbon dioxide, 0.02% of chlorine, and traces of iron, sodium, and sulfate. The distilled water used had been recently boiled to expel dissolved oxygen and carbon dioxide.

Several experiments were carried out with solutions of varying concentrations, and using different amounts of the reacting substances. The general relationships found, however, were the same in all instances and, to economize space, the data obtained from only five experiments are given.

In the first experiment, 8.20 grams of sulfur were thoroughly wetted with water and transferred to a Jena flask, 500 cc, capacity. Two hundred cc. of a solution which, as shown by titration, contained 14.110 grams of

<sup>1</sup> THIS JOURNAL, 27, 244 (1905).

<sup>2</sup> "Sutton's Volumetric Analysis," 9th edition, p. 325.

<sup>3</sup> *Loc. cit.*

dissolved potassium hydroxide, were then added. The flask was connected to a hydrogen generator and pure hydrogen passed in until all of the air had been expelled, in order to prevent any oxidation of the polysulfide formed, to thiosulfate. After the removal of the air, the flask was gently heated for about 4 hours, the temperature of the solution being kept near 50°. At the end of this time, all of the sulfur had gone into solution. While the reaction was taking place, the flask was frequently shaken and a continuous stream of hydrogen passed in. The solution was cooled and transferred quickly to a 500 cc. volumetric flask, avoiding much exposure to the air, made up to the mark with distilled water and analyzed immediately. The results of the analysis are given in the following table.

A second experiment, using 10.000 grams of sulfur and 18.150 grams of potassium hydroxide, was carried out in a similar manner, except that the temperature was kept near 60° and the volume of the solution, while the reaction was taking place, was approximately 400 cc. The results of the analysis of the solution obtained are also given in the table below.

In the third experiment 12.000 grams of sulfur and 22.960 grams of potassium hydroxide were used. The volume of the solution, while the reaction was taking place, was approximately 500 cc. and the temperature near 80°. For the data obtained from the analysis of the solution see the table.

A fourth experiment was tried, in which sulfur was used in excess of that required to unite with the potassium hydroxide present. Eight grams of sulfur were wetted thoroughly and added to 100 cc. of solution which contained 3.678 grams of potassium hydroxide. After the air had been expelled from the flask containing the mixture, it was gently heated until the boiling point was reached; the boiling was continued for a brief time and the solution was allowed to cool. The liquid was then decanted hastily through a rapid filter into a volumetric flask of 250 cc. capacity. The residual sulfur and filter were quickly washed with water until free from polysulfide and thiosulfate, and the filtrate made to volume. The results of the analysis of the filtrate are those given for experiment four.

TABLE I.—COMPOSITION OF SOLUTIONS PREPARED BY HEATING POTASSIUM HYDROXIDE AND SULFUR IN WATER.

	Potassium combined as polysulfide (K). Grams.	Potassium combined as thiosulfate (K). Grams.	Sulfur combined as polysulfide (S). Grams.	Sulfur combined as thiosulfate (S). Grams.	Sulfur combined as sulfite and sulfide (S). Grams.	Potassium hydroxide (KOH). Grams.
Expt. No. 1.....	5.031	2.667	5.980	2.188	trace	3.192
Expt. No. 2.....	6.148	3.073	7.460	2.521	trace	5.025
Expt. No. 3.....	7.315	3.706	8.940	3.040	trace	6.227
Expt. No. 4.....	1.638	0.936	3.302	0.768	trace	none
Expt. No. 5.....	6.205	2.986	7.540	2.449	trace	none

A fifth experiment was made in which 13.122 grams of potassium hydroxide and 10 grams of sulfur were allowed to react in approximately 200 cc. of water. The mixture was kept at approximately 95° until all of the sulfur was dissolved. This required about an hour. The solution was kept under hydrogen as in the preceding experiments. For results see Table I.

#### Discussion of Results.

The ratios of the potassium to the sulfur, in the polysulfide present in the solutions from experiments 1, 2, 3, and 5, are 1 to 1.19, 1 to 1.21, 1 to 1.22 and 1 to 1.21 respectively. The ratios correspond, within experimental error to that of potassium trisulfide ( $K_2S_3$ ) which is 1 to 1.23. The results from the experiments just enumerated also show, that under conditions in which there is an excess of the hydroxide, or merely enough to combine with the sulfur present, the reaction takes place as represented by the following equation:



Variations of temperature (below 100°), and concentration do not affect the nature of the reaction.

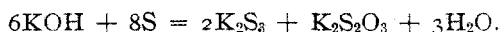
Experiment 4, as well as others not here reported, show that, when an excess of sulfur is used, a secondary reaction takes place in which sulfur, if present in sufficient quantity, combines with the trisulfide to form the pentasulfide ( $K_2S_5$ ). Perhaps the tetrasulfide ( $K_2S_4$ ) is formed as an intermediate product.

In conclusion, it may be well to state that the work on the study of the reaction between sulfur and calcium hydroxide has been nearly completed for some time. Just as soon as some other experimental work, for which there is a more urgent local need, is out of the way, the author hopes to complete this study and present the results for publication.

#### Summary.

1. Methods have been devised which, when used in connection with other well-known methods, may be employed to determine the reaction between sulfur and the alkali and alkaline earth hydroxides in cases where the products of the reaction do not decompose in heated aqueous solution.

2. The primary reaction of sulfur with potassium hydroxide in heated aqueous solutions takes place as represented by the following equation:



3. When sulfur is used in excess, a secondary reaction occurs in which it combines, if present in sufficient quantity, with the trisulfide to form the pentasulfide. Potassium tetrasulfide is perhaps formed as an intermediate product.

4. The variation of temperature (below 100°) and concentration does not alter the nature of the reaction.

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## AN IMPROVED TYPE OF CALORIMETER, TO BE USED WITH ANY CALORIMETRIC BOMB.

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The calorimeters in general use are subject to many errors, namely those of radiation through the surrounding wall, of conduction through the metallic parts and the thermometer, and those due to the inaccuracy of the thermometer readings. Richards<sup>1</sup> has shown that there may be considerable error due to a lack of quick response in the thermometer (the thermometer lag).

The present paper deals with an attempt to eliminate all these errors, through the use of a vacuum cup with a suitable covering, proper precaution having been taken to insulate the different parts.

The vacuum cup has been used by Rubner<sup>2</sup> to show the heat formed by active bacteria, and also recently by Hill,<sup>3</sup> for a calorimeter with which he attempted to measure the heat produced in rats.<sup>4</sup>

Benedict<sup>5</sup> has constructed an adiabatic calorimeter for use with the bomb, which has many advantages over the older styles of calorimeters but it requires a special technique.

*Description of Apparatus.*—In all calorimetric work the rise in temperature, multiplied by the quantity of water affected, gives the calories directly, provided there is no loss or gain in heat. Figure I is a sectional sketch of the bomb and calorimeter, which has been designed. It consists of a bomb, *a*, which may be of any type, of a vacuum cup, *b*, containing water, a stirrer, *j*, and a thermometer, *T*. The stirrer is of the screw propeller type, which is far more efficient than any other.<sup>6</sup> The vacuum cup is of standard size, 14 cm. wide, 30 cm. high, inside measurements, and was obtained through the *Vereinigte Fabriken f. Laboratoriumsbedarf, Berlin, Germany*.

The bomb is of the Kroecker style and, inasmuch as it has two outlets, 4-5, a determination of carbon may be made. The support for the bomb

<sup>1</sup> Richards, Henderson and Freuert, *Proc. Amer. Acad. Arts and Science*, **41**, (1905).

<sup>2</sup> *Arch. Hyg.*, **48**, 260-68.

<sup>3</sup> *J. Physiol.*, **46**, (1913).

<sup>4</sup> Curiously enough, Hill in his computations neglects to take into account the heat lost through the vaporization of water by the animals employed.

<sup>5</sup> THIS JOURNAL, **32** (1910).

<sup>6</sup> U. S. Bureau of Standards, *Circular No. 11*, 1st ed., May, 1911.