4. A mechanism is proposed to explain these results. It can be shown to be in accord also with the results of other experimenters.

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REDUCTION REACTIONS WITH CALCIUM HYDRIDE. I. RAPID DETERMINATION OF SULFUR IN INSOLUBLE SULFATES[1]

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Almost all quantitative methods of determining sulfur in either organic or inorganic matter have as their method of procedure the oxidation of the sulfur to sulfate and subsequent precipitation with barium chloride. With reductive reactions of calcium carbide and calcium hydride in mind it was thought of interest to see whether the sulfur in various compounds, both organic and inorganic, could be quantitatively converted to calcium sulfide by ignition with these substances. If the sulfur were quantitatively changed to calcium sulfide, it could be estimated by acidifying the soluble sulfide solution, followed by iodimetric titration.

The hardest test to which this reasoning could be put was to attempt quantitative reduction of sulfates to sulfides. The amount of soluble sulfide formed was then to be determined with standard iodine solution. The present paper will report results of such experiments.

Sulfur in a steel has long been determined by heating a sample of steel filings with hydrochloric acid in a closed system, dissolving the evolved hydrogen sulfide from the sulfide in the steel in either ammoniacal cadmium chloride or caustic soda solution. The absorbing solution is then diluted with water, acidified with hydrochloric acid and titrated with iodine, using starch as indicator. Soluble sulfides such as calcium sulfide and sodium sulfide may also be determined by iodine titration.

A few investigators have studied reductions of sulfur compounds to sulfides in a quantitative way. Luigi Losana[2] has attempted to reduce sulfur to sulfide by ignition with a mixture of sodium bicarbonate and iron powder. The ignited mass was placed in an evolution flask and treated with acid much as in the determination of sulfur in steel. The method is said to be of general application for inorganic sulfur compounds.

Other metals and mixtures of metals and salts have been tried in effecting conversion of oxy-compounds of sulfur to sulfides. H. Bahr and W. van

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[1] This paper is prepared from the first part of a dissertation on reduction reactions with calcium hydride, to be presented by William E. Caldwell in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Losana, *Giorn. chim. ind. applicata,* **4**, 204–206 (1922).

der Heide[3] used a mixture of barium peroxide and powdered aluminum. B. N. Tiutiunnikov[4] mixed in a heavy infusible glass tube magnesium powder, strips of magnesium ribbon and a sulfur containing substance. Some unpublished work involving sodium fusions with sulfur compounds has been carried on by a colleague.

Experimental

Sulfate Reductions with Calcium Carbide.—Calcium carbide is a more easily obtained and a cheaper compound than calcium hydride. Calcium carbide decomposes upon being heated, yielding metallic calcium and carbon, both in themselves reductive. It was desired to see how complete a reduction of sulfate could be had with powdered carbide. Ebler and co-workers[5] used mixtures of calcium hydride and calcium carbide in partially reducing sulfates in recovering radium from a sulfate mixture; 60–65% reduction is reported on spontaneous fusion.

Commercial calcium carbide is found to contain considerable sulfur, probably due to gypsum occurring with the carbonate from which the carbide is made. A purer, specially prepared carbide was obtained which analyzed 0.034% sulfur. Thus a weighed amount of carbide must be used in the fusions and a correction must be applied to all sulfur determinations. If a carbide free from sulfur were obtainable, it would eliminate a weighing and a correction.

Seven-tenths gram of the carbide was ground to 60-mesh and thoroughly mixed with 0.5 g. of potassium sulfate in a 25-cc. iron crucible. This crucible was heated over a Méker burner and the resultant fusion mass placed in an Erlenmeyer evolution flask for hydrogen sulfide evolution. The evolved hydrogen sulfide was collected in ammoniacal cadmium chloride solution, which was then acidified and titrated for sulfur content with iodine. As water and acid were added to the fusion mass in the evolution flask, acetylene was formed therefrom by action on undecomposed carbide, thus yielding a reducing atmosphere, insuring that no sulfide would be oxidized by the air in the apparatus. Results are given in Table I.

TABLE I

ONE-HALF GRAM OF POTASSIUM SULFATE REDUCED TO SULFIDE WITH CALCIUM CARBIDE

0.5 g. of K_2SO_4 = 0.0915 g. of S

Sample	I_2 titer, cc.	Sulfur equivalent, g.	Reduced S/total S	Reduction, %
1	48.0	0.0768	0.0768/0.0915	84.0
2	48.5	.0776	.0776/0.0915	84.9
3	49.0	.0784	.0784/0.0915	85.8
4	45.0	.0720	.0720/0.0915	79.0
5	46.0	.0736	.0736/0.0915	81.0

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[3] Bahr and van der Heide, *Z. angew. Chem.*, **37**, 848–851 (1924).

[4] Tiutiunnikov, *Chem. Zentr.*, II, 264 (1924).

[5] Ebler and others, *Ber.*, **46**, 2264 (1913).

Quantitative reduction was not obtained. It was attempted to increase the yield of reduced sulfur by mixing sodium carbonate with the calcium carbide, thinking to hold back any escaping sulfur dioxide. When this was done but 60% of the sulfur was reduced to sulfide.

Calcium hydride should have the following advantages over calcium carbide: first, it is more easily obtained free from sulfur; second, evolution of hydrogen sulfide is more readily carried on from hydride residues than from carbide fusion residues, as some free carbon remaining from calcium carbide fusions tends to hold back hydrogen sulfide (it was later found that evolution from calcium hydride fusions residues was unnecessary, acidification of the water solution of the fusion residue, followed by titration, being all that is needed); third, hydrides remaining in the fusion mixture decompose with water to give off hydrogen while carbides with water yield undesirable, odorous acetylene. The hydride might give more complete reduction on fusion with sulfates.

Sulfate Reductions with Calcium Hydride.—Calcium hydride may be obtained from various chemical distributors. It is a light gray solid which may be readily ground in a mortar. All of the calcium hydride used in this work was powdered by means of a small disk grinder and passed through a 60-mesh screen. The grinding must not be too rapid or the heat of friction may cause ignition of the calcium hydride.

Samples of the hydride were tested for sulfur and no trace was detected. The calcium hydride does, however, contain calcium chloride and calcium oxide. The calcium chloride probably comes from the preparation of metallic calcium from which the hydride is made. The calcium oxide is the result of the reaction of the hydride and moisture. In the procedures used neither of these impurities hinder reductive action on sulfates.

Calcium hydride acts on water thus:

$$\begin{array}{lll} CaH_2 + 2HOH = Ca(OH)_2 + 2H_2 & & \\ \text{42 grams} & \text{4 grams or 44,800 cc.} & \\ \text{1 gram} & \text{1,067 cc.} & \end{array}$$

One gram of calcium hydride should evolve 1067 cc. of hydrogen at standard conditions. The purity of the hydride was determined by measuring the hydrogen evolved from a weighed amount. An average of runs indicated that the hydride yielded 803.4 cc. of hydrogen at standard conditions. It is readily seen that we were not dealing with pure calcium hydride but a mixture of calcium hydride, calcium oxide, calcium chloride and probably some sub-hydride of calcium.

A sample of calcium hydride was made in this Laboratory by passing hydrogen over rasped calcium, heating in a pyrex tube to about 500° in a small electric furnace. This product was a light gray, easily ground solid, comparable to that obtained on the market. It also yielded much less than the theoretical amount of hydrogen on treatment with water.

As moisture was kept from the product and since very little chloride is present, the deficiency in amount of evolved hydrogen is probably due to a sub-hydride of calcium.

Fusions for sulfur estimation were made upon purified sulfates of potassium, barium, strontium, calcium and lead. The comparisons of these results with the theoretical are listed in later tables. Carefully standardized 0.1 *N* iodine and sodium thiosulfate solutions were used in titrations.

Of the various methods of procedure that were tried for running sulfur determinations on sulfates, starting by ignition with calcium hydride, the following outlined process gave the best results.

One-half or 0.25 g. sample of the crushed sulfate were mixed in a 25-cc. iron crucible with about 7 g. of powdered calcium hydride. This amount of hydride about half fills the crucible. Mixing is accomplished with a spatula; about thirty turns of the spatula are deemed sufficient. A surface layer of hydride is placed above this mixture to the depth of one-eighth inch.

A cover is placed on the crucible and the whole quickly heated over the full blast of a Méker burner and then allowed to stand in the full flame for ten to fifteen minutes. After cooling, the cover is removed, and if heating has not been too high, the residue is easily jarred from the crucible as one solid lump, which can then be broken up and transferred from a piece of paper into an Erlenmeyer flask of 500-cc. capacity.

Above the Erlenmeyer flask is placed a short reflux condenser, the upper end of which is closed by a two-holed rubber stopper. Through one hole of the stopper is inserted a 100-cc. dropping funnel. A bent glass tube for the escape of evolved hydrogen passes through the other. Water is slowly dropped upon the fusion residue until the excess hydride is broken up, much hydrogen being evolved the while. More water is added and a milk-like solution of calcium hydroxide and calcium sulfide is obtained. This is transferred to a liter beaker, diluted to 400–500 cc. and acidified with 100 cc. of concd. hydrochloric acid, allowing the heavier acid to run down the side of the beaker and not stirring. Stirring of the solution at this point means a loss of considerable hydrogen sulfide.

The beakers are allowed to stand for a few minutes and the solid matter therein dissolves in the acid. A clear solution will not always result but the turbidity will not interfere with the very pronounced starch–iodine end-point. The solution is now titrated with iodine, stirring gently at first, with starch solution as indicator. One cubic centimeter of the 0.1 *N* iodine is equivalent to 0.0016 g. of sulfur.

On the delicacy of this end-point it has been found the accuracy of the method depends. The end-point is not all that is to be desired as a little excess iodine is needed to yield a starch–iodine color to the whole solution. If the samples taken are too large, an overabundance of colloidal sulfur is formed which occludes some iodine and tends to lower results. It is well to add a slight excess of iodine and titrate back with standard sodium thiosulfate. With a little practice the end-point can be judged to less than one-half of a cubic centimeter, which is less than 0.0008 g. of sulfur. This would correspond to 0.15% sulfur in a 0.5-g. sample and is then the accuracy of the method. Results of analysis of potassium sulfate are given in Table II.

Samples 1–4, inclusive, are seen to give close approximations to the true sulfur content of the sulfate. These samples were treated as has been outlined.

Samples 5 and 6 were run as the others except that vigorous stirring

TABLE II

0.25 G. OF POTASSIUM SULFATE REDUCED TO CALCIUM SULFIDE WITH CALCIUM HYDRIDE

Sample K_2SO_4 = 18.37% sulfur

Sample	Iodine titer, cc.	Sulfur equiv., g.	Sulfur, %	Sample	Iodine titer, cc.	Sulfur equiv., g.	Sulfur, %
1	28.5	0.0456	18.24	5	22.0	0.0352	14.08
2	28.5	.0456	18.24	6	23.0	.0368	14.72
3	28.5	.0456	18.24	7	20.0	.0320	12.80
4	29.0	.0464	18.56	8	18.0	.0288	11.52

was carried on when acidifying the solution of the fusion residue. During this stirring the odor of hydrogen sulfide was noticed coming from the liquid and the iodine titer is quite low.

Samples 7 and 8 show the result of insufficient heating. It is not enough merely to heat until after a potassium flare is seen. The whole crucible must be heated to redness and kept in the full flame for several minutes. Fusion samples that were properly heated at redness for several minutes were tested for undecomposed sulfate and gave a negative test. The reduction is therefore quantitative. Any partial decomposition resulting in sulfite formation would not change results as the sulfite uses up iodine to the same extent as soluble sulfide. Little or no sulfite remains, however, as hydrogen sulfide may be evolved from fusion residues equivalent to all of the sulfur present. Results of analyses of barium, strontium and calcium sulfate are given in Tables III, IV and V.

TABLE III

0.25 G. OF BARIUM SULFATE REDUCED TO SULFIDE WITH CALCIUM HYDRIDE ($BaSO_4$, 13.6% OF SULFUR)

Sample	1	2	3 (0.5 g.)	4
Iodine titer, cc.	21.5	21.5	42.5	21.5
Sulfur equiv., g.	0.0344	0.0344	0.0680	0.0344
Sulfur, %	13.76	13.76	13.6	13.76

TABLE IV

0.25 G. OF STRONTIUM SULFATE REDUCED TO SULFIDE WITH CALCIUM HYDRIDE ($SrSO_4$, 17.12% OF SULFUR)

Sample	1	2	3 (0.3 g.)
Iodine titer, cc.	26.5	26.5	32.0
Sulfur equiv., g.	0.0424	0.0424	0.0512
Sulfur, %	16.96	16.96	17.07

TABLE V

0.25 G. OF CALCIUM SULFATE REDUCED TO SULFIDE WITH CALCIUM HYDRIDE ($CaSO_4$, 23.55% OF SULFUR)

Sample	1	2	3 (0.3 g.)
Iodine titer, cc.	37.0	37.0	44.0
Sulfur equiv., g.	0.0592	0.0592	0.0704
Sulfur, %	23.68	23.68	23.46

Runs were attempted fusing 0.25 g. of lead sulfate with calcium hydride and treating as in the case of the other sulfates. The following reactions undoubtedly occur.

$$PbSO_4 + 4CaH_2 = PbS + 4CaO + 4H_2$$
$$CaH_2 \leftrightarrows Ca + 2H$$
$$Ca + PbS = CaS + Pb$$

This free lead is only slowly acted upon by the hydrochloric acid which is added prior to iodine titration. As a consequence iodine end-points are fading and results are high. An attempt was made to evolve hydrogen sulfide from the fusion residue as in determining sulfur in steel. The metallic lead as it dissolved, however, formed insoluble lead sulfide and thus held back some sulfur.

The method as outlined, then, is only applicable to non-volatile sulfur compounds free from metals which form acid-insoluble sulfides. Work is being carried on making calcium hydride fusions with volatile sulfur compounds in bombs.

Discussion of Results.—Probable chemical equations for the action of calcium hydride on any sulfate are as follows

$$MSO_4 + 2CaH_2 = MS + 2CaO + 2H_2O$$
$$MSO_4 + 4CaH_2 = MS + 4CaO + 4H_2$$

Since calcium hydride decomposes to some extent around 700°, it was thought that secondary reactions might occur

$$CaH_2 \leftrightarrows Ca + 2H$$
$$MS + Ca = CaS + M$$

Experiment verifies these last reactions even to the replacement of sodium and potassium by calcium. When potassium sulfate and calcium hydride ignitions were being made a potassium flare was noticed. When fusions of sodium thiosulfate and calcium hydride were made a sodium flare resulted. On examining the cover of the crucible after these latter fusions it was noticed that some sodium metal had condensed on the cooler cover, forming small globules.

It is evident from the tables that the method gives a quantitative estimation of sulfur in alkali and alkaline earth sulfates.

Insoluble alkaline sulfates are commonly determined for sulfur content by initial fusion with sodium carbonate to decompose the sulfate, followed by extraction of the sodium sulfate formed, ultimate precipitation of barium sulfate, and necessary filtering, drying, igniting, weighing and calculating. By the method herewith outlined sulfur may be estimated in insoluble sulfate samples within forty minutes.

Calcium hydride may be readily obtained and is easily powdered. It is a rather expensive chemical at present in that there is little demand for it in quantity. The cost of 7 g. of the hydride, or enough for one fusion, is about thirty-five cents. The saving of time and labor is the main merit of the method.

Summary

1. Calcium carbide has been studied as a reductant for sulfates. It is not as effective as calcium hydride.

2. Calcium hydride presents itself as a reagent for the quantitative reduction of alkaline earth and alkali sulfates to sulfides. From such fusion residues sulfur may be determined by iodine titration.

3. An example is given of replacement of potassium and sodium by calcium.

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[CONTRIBUTION FROM THE FOOD RESEARCH LABORATORY AT THE MEDICAL COLLEGE OF THE STATE OF SOUTH CAROLINA, CHARLESTON]

THE POTATO AS AN INDEX OF IODINE DISTRIBUTION[1]

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The theory that endemic thyroid enlargement is caused primarily by lack of iodine has been quite generally accepted by American scientists, so that studies on the occurrence of iodine in human environment are of considerable interest. McClendon and Williams[2] have shown that there is a correlation between shortage of iodine in surface water supplies and the incidence of goiter.

Numerous analyses by these and other workers have established that places in the United States where the water contains more than two parts per billion of iodine are few, and more than five parts per billion exceedingly rare. Von Fellenberg[3] concluded, as the result of an extended metabolism trial on himself, that the daily iodine requirement for a man is 14 micrograms, which is a great deal less than the amount (300 to 400 milligrams per year) recommended by Kimball[4] for goiter prophylaxis in the United States. Even if inorganic compounds of iodine are efficiently utilized in the body, water alone cannot supply the requirement in more than a very restricted area. Hence McClendon[5] turned his attention to vegetable foods, and was able to show that foods from Maine and Connecticut contain more iodine than do those from Minnesota or Oregon.

The senior author of this paper[6] has called attention to the relatively large amounts of iodine present in root and leafy vegetables from South Carolina, analytical data for which are now presented in Table I, and

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[1] Presented before the Division of Agricultural and Food Chemistry at the 77th meeting of the American Chemical Society, Columbus, Ohio, April 29–May 3, 1929.

[2] J. F. McClendon and Agnes Williams, *J. Am. Med. Assocn.*, **80**, 600 (1923).

[3] Th. von Fellenberg, *Biochem. Z.*, **142**, 246 (1923).

[4] O. P. Kimball, *J. Am. Med. Assocn.*, **91**, 454 (1928).

[5] J. F. McClendon and J. C. Hathaway, *ibid.*, **82**, 1668 (1924).

[6] Roe E. Remington, *Science*, **68**, 590 (1928).